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Rayon Reports

Prepared Monthly by American Viscose Corporation, New York, N. Y. JULY, 1951

Avisco Develops Springier Rayon Staple for use in both Apparel and Upholstery

To meet the need for a springier and coarser rayon staple for apparel and upholstery uses, Avisco has developed an 8-denier crimped staple. This new product has a bouncy hand approximating wool 58-60's. It rounds out the rayon staple line by filling the vacant niche between 5½-denier, the coarsest apparel staple made up to now, and 15-denier carpet staple.

A Variety of Uses

Men's and boys' sweaters, bath mats, upholstery and drapery fabrics, all made entirely of 8-denier rayon staple, are in limited commercial production. Other suggested uses, both for 100 per cent and for blends, are in men's hosiery, slacks, suitings, blankets, hand-knit yarns, knitted and wooly-type neckwear and terry cloth.

Stiff, bristly effects are possible, similar to those obtained with mohair and coarse apparel wools. The new, 8-denier staple has been blended experimentally with mohair in frieze and plush fabrics, and the results have been highly satisfactory.

Greater Resiliency Achieved

Considerably more resiliency results from use of the new staple than may be obtained with 3- or 5½-denier rayon staple. The fabrics made with 8-denier staple cannot be approached with either finer rayon staple or with cotton. On the other hand, bath mats and throw rugs made with it are soft and luxurious.

Exceptional wearing qualities are indicated by preliminary wear and abrasion tests. Use tests are under way, but have not been completed.

Among the many advantages of the 8-denier rayon staple is that it can be spun on the cotton as well as the worsted and woolen systems.

The applications now in limited commercial use include yarns spun of 100 per cent 8-denier staple on all three systems.

Limited Production at Present

Production is on a pilot-plant scale, and probably will remain so for some time. Avisco is not seeking to market it now, since commercial production would have to be at the expense of other sizes, the demand for which exceeds the company's productive capacity. The corporation is interested, however, in encouraging experimental work with limited quantities, as it believes the future possibilities of 8-denier rayon staple are great.

Inquiries are invited. Address: American Viscose Corporation, Rayon Staple Sales, 350 Fifth Avenue, New York 1, N. Y.

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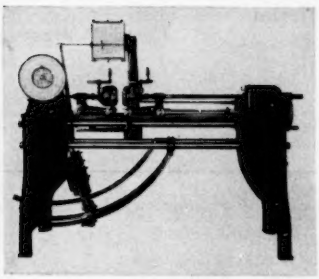

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TEXTILE RESEARCH JOURNAL

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The Relationship Between the Structural Geometry of a Textile Fabric and Its Physical Properties

Part II: The Mechanics of Fabric Abrasion*

Stanley Backer†

This paper is primarily concerned with the mechanics of textile fabric abrasion. However, considerable attention is devoted to the theory of friction and the theory of cutting of crystalline solids. This is intended as a framework for the study of visco-elastic fibrous materials. Such an approach seems logical in view of the significant part which both the elastic and plastic properties of metals play in the phenomena of rubbing and cutting. It is particularly significant that these studies on metals often report the use of solid high polymers as models and experimental materials.

It has taken over 100 years of research on the part of physicists and engineers to determine the nature and causes of friction in crystalline solids, and only in the last 15 years have they made progress in the study of surface cutting. Within the last few years several workers in the field of fibrous high polymers have recognized the applicability of the findings of crystalline-solid research as related to the study of friction, but no one in the fiber field appears to have profited from available information dealing with surface cutting. It would seem that more use should be made in textile research of the experimental techniques and the analytical conclusions of previous investigators in the more general field of solid bodies.—Editor.

Introduction

There is a need to differentiate between the terms "serviceability" and "abrasion-resistance" of textile fabrics. The term "serviceability" should relate to the over-all durability of textile materials under conditions of intended use. "Abrasion-resistance," on the other hand, should be restricted in meaning to the ability of a fabric to withstand direct rubbing under conditions of intended use. Papers published on the subject of abrasion-resistance before 1942 were, for the most part, limited to reporting the results of laboratory rubbing tests. The lack of information on field performance with respect to abrasion can be attributed to the time and expense involved in accumulating valid service data or carrying out controlled field tests. These deterrents were disregarded in 1942 because of the

* Part I (a literature review) appeared in the November, 1948, issue of TEXTILE RESEARCH JOURNAL.

† Textile Division, Massachusetts Institute of Technology.

military and economic pressure for more durable materials, and there have since been reported a number of experiments in which controlled field-test data are available [28, 29, 60, 61]. These experiments furnish strong evidence of the improvement in the abrasion-durability of textile products which can be achieved through structural design and special cloth finish.

As a major consumer of textile materials, the Quartermaster Corps of the U. S. Army faced the need for improving the abrasion-resistance of fabrics used in combat clothing, thus postponing failure of the garment as a result of mechanical attrition. The Army program of research and development relating to this problem has been outlined and its connection with similar civilian research has been stressed [1, 30].

The results of this work have been highly gratifying in that the fabrics developed as a part of the program were shown in controlled field tests to be from 50% to 200% more durable than the standard cloth used for the fatigue garment of ground troops. In some instances blends of fibers were used with a view toward reinforcing weak points in cloth structures. In other cases, carded yarns were substituted for combed yarns, weave was modified, texture was changed, or yarn size was varied. Procurement choice of fabrics demonstrating improved abrasion-resistance took into consideration three additional factors: availability—*i.e.*, production rate and source of raw material; cost; and retention of other desirable characteristics—in particular, lightness and tear-resistance. Fabrics meeting all three criteria were developed with 50% to 75% increase in abrasion life over the previous procurement standard. Information on construction details of such materials is now available in the form of procurement specification and is therefore not included here.

During the Army's extensive program on abrasion-resistance, considerable light has been thrown on the role of fabric structure in the mechanism of rubbing attrition. As a result of such clarification, it is believed that the basis for the improvements referred to above can be generalized and applied in the case of other types of fabrics. The present paper discusses the geometrical aspects of fabric abrasion and points out the areas of the problem which require further investigation. The material presented is by no means the product of Army laboratories alone, but includes the effort of contracting laboratories working within the scope of the program.* The report will further attempt to piece the pertinent experience of Army laboratories and field-test groups into the background of information on abrasion-resistance available in the literature. Accordingly, where detailed data are furnished it may be assumed, unless otherwise stated, that their source is the Quartermaster Laboratory, Philadelphia, or the Combat Course at Camp Lee, Virginia. Where such specific data are not available, the discussion of elements of the mechanism will admittedly assume a philosophical approach, but this is essential in order to provide a complete theory and it is hoped that it will have direct heuristic value.

Mechanism of Cloth Attrition

It is recognized that textile fabrics are not homogeneous isotropic materials. Instead, woven cloth represents a two-phase system of air and fiber, wherein each fiber, anisotropic in nature and of a length which may reach, as in the case of cotton fibers, several thousand times its diameter, is helically twisted into a cylinder of varying hardness with other rod-like fibers which differ somewhat in length, diameter, cross section, and morphology. The twisted structure is then laid in an essentially horizontal plane, parallel to other yarns, and is laced orthogonally with a set of similarly constructed threads. Through the use of various combinations of cylindrical diameters, spacings, and manner of interlacing, numerous factors of orientation and geometry can be introduced to ensure that the fabric does not behave mechanically like the bulk material of which it is chemically constituted. All this serves to complicate the total mechanism of cloth attrition through rubbing as compared to the surface abrasion of solid materials. But there is compensation in the fact that the geometrical elements introduced assume a major role in the abrasion mechanism and enable the investigator, under certain conditions, to disregard the elements involved in the wear of solid bodies and to deal first with the easily controlled factors of fabric structure.

Consider first the action which takes place when a protuberance of a foreign surface comes in contact with the surface of the fabric. The term "pro-

* Textile Research Institute, The National Bureau of Standards, Institute of Textile Technology, Fabric Research Laboratories, and The Textile Division of The Massachusetts Institute of Technology.

tuberance" is used loosely and implies both a microasperity in the case of a smooth surface and a grit in the case of a rough abrasive surface. Single fibers touched by the projection of the foreign surface will act in different ways, depending upon the nature of the contact:

1. By reason of firm anchoring in the fabric and hard backing of the other fibers in the yarn, the fiber will be subjected to frictional wear such as occurs when smooth metal surfaces are rubbed together. Wear of this type will take place when the foreign body is quite smooth—say, for example, the surface of polished furniture.

2. Where surface projections of the abrading surface are small relative to the diameter of the fiber, but are nevertheless quite sharp, the fiber will be subjected to a surface-cutting process such as occurs in metal cutting or grinding. Such wear will occur when a very fine abrasive or emery surface is rubbed across a fabric.

3. Where the surface protuberances of the abradant are large compared to fiber diameter and the normal forces between the abradant and cloth planes are high, the fiber will be plucked much like a violin string is plucked by the finger of a musician. This plucking develops components of force along the fiber axis of higher magnitude than those imposed in the direction of the relative motion (as a result of the geometry of the force system). Release of these axial loads may take place by rupture of the stressed fiber, or by its slippage from the body of the yarn, or by its vertical displacement beneath the path of the abradant protuberance.

Here are represented elements of direct frictional wear, surface cutting, and fiber rupture or slippage. The nature of the abrading surface and the normal pressures of the rubbing determine which is the more severe under a given set of conditions. However, the mechanism of fabric abrasion is not as simple as has been pictured. Consider, for example, the fact that the forces developed in the plane of the material as a result of either friction or cutting develop, in turn, components along the fiber axis and thus contribute to axial tensile or bending rupture or to fiber slippage in the yarn structure. Fiber slippage, cracking in bending, or tensile rupture may take place suddenly on first contact of the fiber with protuberances of the abradant, or may follow repeated abrasive stress applications involving dynamic fatigue of individual fibers. It follows that pure friction and cutting may have an indirect effect on fabric wear which may exceed in magnitude the direct effect. The fact remains that the infinitesimal quantities involved in direct frictional wear have limited the accumulation of experimental results regarding its mechanism, although recently developed electron microscope and tracer techniques [49] are helping to correct the deficiencies of past investigations. For this reason we shall avoid general consideration of the factors of direct frictional wear, and shall consider the mechanics of friction with a view toward understanding the nature of its indirect effects in fabric breakdown.

Frictional Phenomenon

Indirect frictional wear is caused by the axial components of surface frictional forces. The magnitude of these forces is generally not related to the severity of *direct* frictional wear. Engineers [49] concerned with the wear of metals state that only a minor portion of frictional energy goes into *direct* wear. The major avenue of dissipation of frictional energy in metals is through transformation into thermal energy, immediately or upon recovery of the elastic strains incurred during rubbing. In the case of abrasion of fabrics, however, it is easily seen that the magnitude of the frictional forces developed will be geometrically related to tensile forces set up along the fiber axis and therefore to the damage occurring through fiber tensile and bending fatigue and slippage (all other factors being held constant). On the other hand, friction between fibers acts to control fiber slippage and thus reduces abrasive damage through this mechanism. For these reasons it is desirable to consider the nature of friction as studied in solid bodies, as a prerequisite to understanding its role in damage to fabrics during rubbing [9, 10, 27, 50].

It has been generally observed that frictional resistance—that is, the spontaneous force which resists relative motion between two bodies in contact—depends only upon the normal load at the interface between the bodies, and is independent of the apparent area of contact. This was first pointed out and verified experimentally by Leonardo da Vinci in the 15th century. In 1781 Coulomb repeated da Vinci's experiments and confirmed their results. He was the first to differentiate between static friction and kinetic friction, and he showed that the latter was the smaller (of the order of one-third

of the static frictional resistance) and, further, was nearly independent of speed. Since Coulomb, numerous mechanisms of friction have been proposed to explain the general laws of friction—*i.e.*, direct dependence on load and independence of geometric area of contact and speed. Of these, three merit consideration: the surface roughness hypothesis; the adhesion hypothesis; and the ploughing hypothesis.

Surface roughness and the mechanical interlocking of surface protuberances were considered by de la Hire [16], and later by Coulomb [15], to cause frictional resistance to motion between surfaces in contact. These rough spots were considered to make an average angle, θ, with the plane of the surfaces. The horizontal force, F_o, needed to push the weight, W, of the upper body up such an average inclined rough spot, considered to be frictionless, was:

$$F_o = W \tan \theta.$$

Here, what appears to be frictional work is actually the work required to raise weight W. This equation was in agreement with the generally observed laws of friction. However, in later years the development of improved devices for studying surface irregularities and measuring the relative motion between bodies enabled investigators to show that friction did not vary systematically with roughness [24] and that relative vertical motion between sliding planes was much less than the vertical heights of the two surfaces [62]. One might wonder what happens to the energy to be regained when the weight is sliding down the other side of the frictionless hill. Further, it is questionable whether surface protuberances occur with any degree of regularity [65, 66, 69], and therefore it is improbable that uniform interlocking of hills and valleys takes place. The hypothesis is seen to have some validity in the case of surfaces having uniformly spaced macroprotuberances. Nevertheless, there are still ardent supporters of the roughness hypothesis as applied to the general case of friction [5].

The second mechanism, that of adhesion, has been more generally accepted by students of friction and wear. Hardy [24] was among the first to clarify the concept of molecular adhesion as the dominant friction mechanism, and quantitative expressions for its effect were proposed by Tomlinson [67]. Later, Holm [27], Merchant [34], and Bowden [9] developed the theory so as to relate frictional behavior to the mechanical properties of the bodies involved in sliding. The theory proposes that when the two bodies are rubbed together, the atoms of the protuberances of upper and lower surfaces are moved into each other's electrostatic field of attraction (a spacing of less than 2×10^{-8} in.) and thus form minute welds or adhesions. Continued movement of the surfaces requires additional force to rupture these adhesions. The elastic energy released at the rupture results in rapid vibration of surface and subsurface atoms and is finally dissipated in the form of heat.

In engineering terms, the force required to shear the local adhesion depends upon the shear resistance, S, of the materials involved (that is, of material A or B or bond A—B) and the true area, A_t, of such contact points:

$$F_s = S \cdot A_t.$$

The true area, A_t, has been found to depend upon the total load [9, 27] between surfaces and upon the mean resistance of local asperities to plastic flow, p_m (under normal pressure), since

$$A_t = W/p_m.$$

Here we see that apparent area of contact does not enter into the determination of frictional force:

$$F_s = S \cdot W/p_m.$$

Since S and p_m are constants of the material, the relationship shown above is in agreement with the general laws of friction as long as the ratio S/p_m remains unchanged with speeds of rubbing. Numerous experimental verifications of the adhesion theory [9, 10, 27] have established its utility in all problems of friction, including studies of nonmetallic bodies.

The third mechanism of friction, involving ploughing of a soft surface by a hard one, has been proposed by Bowden and Tabor [9]. These investigators have shown that the force, F_p, required to plough a hard asperity along the surface of a soft material is dependent upon the projection of the asperity on the plane normal to direction of motion, A_p, and the average flow pressure, p_m, of the softer material—*i.e.*,

$$F_p = A_p \cdot p_m.$$

It should be noted that while the damage of direct frictional wear, mentioned briefly above, implies interchange of material between surfaces (in one or both directions), considerable damage may occur as a result of ploughing without interchange of

material. This damage may be regarded as affecting surface smoothness and appearance or ability of the ploughed body to withstand subsequent dynamic stresses in service.

The above three elements of frictional force can be added, in the most general case, to determine the total force, F_t, which resists sliding between the two surfaces thus:

$$F_t = F_o + F_s + F_p = W \tan \theta + SW/p_m + A_p p_m.$$

Since the coefficient of friction, μ, is defined as the ratio between frictional resistance and normal force, there follows:

$$\mu = F_t/W = \tan \theta + S/p_m + A_p p_m/W.$$

The above expression for the frictional force, F_t, does not contain quantities involving speed of sliding or geometrical area of contact, and it therefore satisfies the second and third laws of friction. The third term on the right, $A_p p_m$, does not contain the quantity W and therefore violates the first law, which states that the frictional force is directly related to the normal load. However, in the case of smooth surfaces, this term is generally quite small. Where sharp asperities are present, the resulting cutting and ploughing action promotes direct abrasive damage which far exceeds the indirect effects of the frictional force F_t as influenced by the last term $A_p p_m$.

Surface Cutting

Sharp protuberances of an abradant in contact with a fiber lying on the surface of a fabric will act to cut the fiber. Such cutting develops a complex stress pattern within the individual fiber. To analyze this pattern one must know the mechanical properties of the fiber. Unfortunately, studies of this sort have been limited mostly to considerations of tensile behavior [31, 36, 38, 39, 44, 63]. A few papers report on the torsional characteristics [37, 41, 58], on bending [64], and on the shear strength [19] of fibers. Because of the paucity of information on complex stresses in fibrous high polymers, we are compelled to deal with other polymers available in bulk or sheet form—for example, the plastic models used to study stress distributions in engineering studies of metal cutting and grinding. The validity of the model technique is dependent upon the fact that stress distribution in a homogeneous isotropic elastic medium is dependent upon boundary stress conditions (plane) and is independent of the nature of the material as long as its elastic limit is not exceeded. This condition limits the applicability of quantitative relationships derived in the field of metals and isotropic polymers, but the qualitative aspects of these relationships warrant careful review before experiments with anisotropic materials are attempted.

Stress Relations in Isotropic Materials

Michell's [40] solution for the radial stress distribution resulting from the action of an infinitely sharp point pressed against the edge of an infinite plate of an elastic isotropic material illustrates the basic stress pattern to be expected in the cutting of a bulk plastic. Using polar coordinates, the field stress is resolved into a radial normal stress, σ_r, a tangential normal stress, σ_t, and a shearing stress, τ_{rt}, as illustrated in Figure 1 (top), and the distribution is seen to be:

$$\sigma_r = -\frac{2P}{\pi r t} \cos \theta; \quad \sigma_t = 0, \quad \tau = 0.$$

It is further shown that the loci of points of equal principal shear stress, which are termed isochromatics in photoelastic studies, form a set of circles passing through the point of application of the concentrated force, with centers on the line of the thrust (Figure 1 (bottom)). The same solution is applicable to the case of the concentrated force applied at an incline to the surface normal, provided θ is taken as the angle between the force direction and the radius, r. These stress distributions have been plotted by Coker and Filon [13] and verified photoelastically using a thin sheet of celluloid. More recently, Frocht has furnished [20] striking illustration of the agreement between photoelastic and theoretical stress patterns for an inclined concentrated load on a semi-infinite plate. In their treatise on photoelasticity, Coker and Filon illustrate similar isochromatic patterns which occurred during the cutting of Xylonite with a high-rake-angle tool. These same patterns have been observed by the present author in the cutting of Lucite with a modified milling machine, except at the point of the tool, where excessive plastic yield gave anomalous photoelastic results. Since the Lucite specimen used in this experiment was isotropic, a sheet of oriented cellulose acetate was subjected to a concentrated normal load applied at an edge which corresponded to the direction of orientation. The resulting isochromatic pattern

for the anisotropic sheet is pictured in Figure 2; if allowance is made for the wedge penetration, it resembles quite closely the theoretical stress pattern plotted in Figure 1 (bottom) for elastic isotropic material. It remains to extend this work to specimens of much higher orientation and, eventually, to fibers before use of such stress data becomes useful in interpreting the mechanism of the cutting and abrasion of textiles.

As Nadai [42] points out, the lines along which the principal shearing stresses act, the trajectories, do not correspond to the isochromatic lines shown in Figure 1 but, rather, intersect the isoclinics of the system at an angle of 45°. (For information on the photoelastic techniques and terminology involved see [13, 20].) The isoclinics may also be determined photoelastically by rotating the specimen in the polarized field. The trajectories of the principal shear stress are of considerable importance for they coincide (in the case of many isotropic materials) with the slip lines, which appear, for example, in the case of a piece of mild steel stressed to the plastic limit.

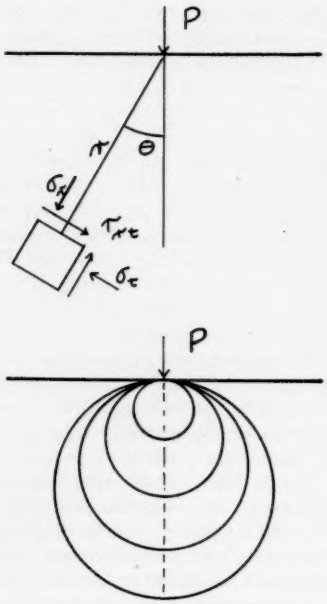

FIG. 1. *Stress distribution resulting from a concentrated load applied at the edge of an infinite plate.* Top—*Stresses on an element at a distance* r *from point of contact.* Bottom—*Isochromatics, or lines of constant principal shear stress.*

Consider now the general process of cutting crystalline materials. The currently accepted mechanism of cutting was first proposed by Piispanen [45], and involves the successive displacement of a series of shear layers in a manner similar to the slippage of cards in a pack. The chips (either continuous or discontinuous) formed in this process advance up the edge of the tool under considerable normal pressure and their motion is opposed by frictional forces at the chip tool interface. The dynamics of this mechanism have been worked out in considerable detail by Merchant [35] and provide relationships between the forces developed during cutting, the geometry of the tool, and the mechanical properties of the material being cut. It should be pointed out that vertical forces developed during cutting are of importance in the abrasive wear of high polymers for they determine the extent of downward deflection of the material being cut and, consequently, the depth of the cutting damage. The horizontal forces measured during cutting are significant in that they are related directly to the axial component of fiber stress which develops and therefore to the extent of fabric damage in the form of fiber slippage or fatigue (see Figure 3).

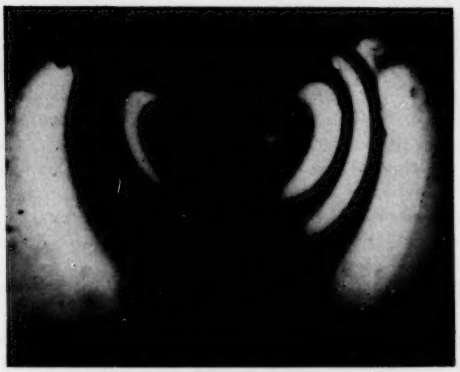

FIG. 2. *Sheet of oriented cellulose subjected to a concentrated normal load applied at an edge, shown between crossed Nicols. Direction of orientation is horizontal. Magnification, 150×. Dark brush originating at apex of concentrated loading wedge and spreading downward is isoclinic; this disappears upon insertion of quarter-wave plate and conversion of sodium beam to circularly polarized light, thus leaving concentric circular arcs.*

In particular, it can be shown that:

$$F_s = TA/\sin\phi$$
$$F_v = TA \sin(\beta - \alpha)/\sin\phi\cos(\beta + \phi - \alpha)$$
$$F_h = TA \cos(\beta - \alpha)/\sin\phi\cos(\beta + \phi - \alpha),$$

where F_s = the shear force on the slip plane; F_h = the horizontal force on the tool; F_v = the vertical force on the tool; T = the shear stress developed along the slip plane; A = the cross-sectional area of the work being cut by the tool; ϕ = the angle between the shear or slip plane and the horizontal; β = the angle between the resultant force on the tool and the tool face; α = the rake angle of the tool.

Merchant [35] has shown by further analysis of conditions of minimum energy of cutting that:

$$\phi = 45° - (\beta - \alpha)/2.$$

The relations derived by Merchant for metals have been applied with success to the cutting of plastics. In only one point does an anomaly occur and that is on the question of a definite shear plane at which all shear takes place. That this occurs in metals is strikingly illustrated on polished and etched cross sections of partially formed chips such as are presented by Merchant [35]. Preliminary experiments on the part of the present author indicate that the occurrence of a definite shear plane depends upon the mechanical properties of the bulk plastic and the geometry of the tool. Cutting of highly plasticized Lucite with high rake angles was observed under a microscope, and a general wedge-shaped area over which shear occurred gradually was seen. Lucite specimens with lower plasticizer content and cut with smaller rake angles showed a sharp plane at a definite angle from the tip of the tool.

Experiments by Cook and Howitt [14] using wood illustrate that the metal cutting mechanism appears to apply to anisotropic material when the material is so oriented that its direction of minimum shear strength is roughly oriented in the direction of the shear plane of metal cutting. In the case of wood this means cutting across the grain. However, when wood is cut parallel to the grain, the tool acts as a wedge, prying up the individual grain, cantilever fashion, until rupture in bending occurs well in advance of the tool tip. Separation of the grain from the bulk of the material is mainly through tensile rupture of the intergrain bond. The chip so formed may be discontinuous, with straight sections and sudden bends where the cantilever has yielded locally.

The dynamics of metal cutting have been extended to the case of grinding by Backer, Marshall, and Shaw [3, 33], a step which has brought to light factors of considerable importance in the field of strength of isotropic materials. This latter work is most pertinent to the subject of abrasion damage to fibrous high polymers for it deals with the micro-damage caused by passage of sharp particles across the surface of a bulk material. It is likely that results observed by these investigators can be

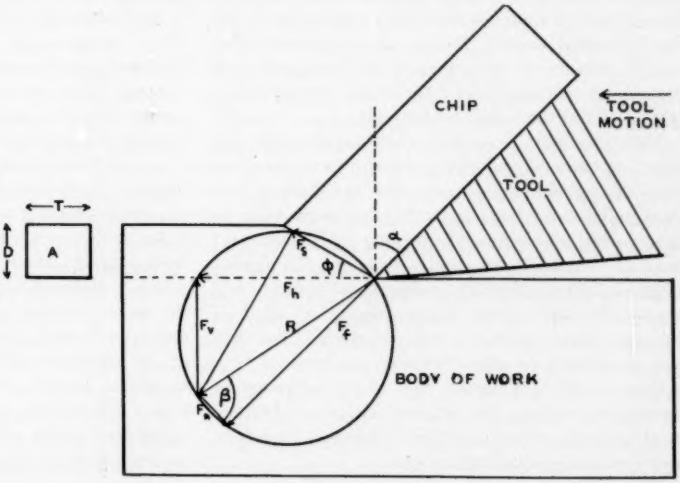

FIG. 3. *Diagram of forces developed during cutting. Rake angle, α; shear angle, ϕ; coefficient of friction, tan β; horizontal force, F_h; vertical force, F_v; force on the shear plane, F_s; force normal to tool face, F_n; force along tool face, F_f; cross-sectional area of the work being cut by tool, A; work thickness, T; depth of cut, D.*

applied to cases of fiber and yarn abrasion where the abrasive asperities are small relative to the fiber diameter.

Surface Cutting of Fibers

Harsh abrasion and surface cutting of individual fibers in actual service have been well pictured by Clegg [12] in a most comprehensive microscopic study of the mechanism of wear. In carefully drawn and colored sketches Clegg shows the nature of abrasive attrition of representative fibers taken from different fabrics and garments under varying conditions of use. In the case of cotton fibers held firmly in the fold of a starched collar, Clegg demonstrates the effect of abrasive action on the fiber cuticle followed by a loosening and breakdown of the fibrillar structure. Similar failure is noted in other cotton fabrics where surface fibers of protruding yarns are held firmly by fabric structure or light starching and, accordingly, receive intense abrasion. Striking drawings are also furnished of wool and silk fibers which have been subjected to abrasive action resulting in mechanical attrition at the surface and subsequent loosening of the internal cell or fibrillar structure, respectively. Only in the case of viscose and acetate rayons does Clegg show complete attrition of fibers without visible signs of fibrillation. This last observation is probably dependent upon the nature of attrition to which the fiber has been subjected, for Best-Gordon [4] gives positive evidence of the distinct barbed effect on the surface of spun viscose fibers caused by severe mechanical abrasion. In fact, the existence of this barbed surface in the presence of fiber and yarn movement within the fabric leads to significant felting of the spun viscose material.

This carefully executed work emphasizes the effect of the cell and fibril structure on abrasive-wear damage and subsequent fiber breakdown, and thus points to a need for extending such work as that on the mechanics of grinding to laminar and even fibrillar submicroscopic structure. A significant step in this direction is illustrated in Schiefer's studies [53, 54] of the disintegration of wool in abrasion tests, where it was concluded that the coating formed on the abradant consisted of "extremely small particles of wool which appeared to correspond in shape and size to the elemental structural units (keratin molecules) proposed in recent concepts of the structure of wool."

Axial Forces and Tensile Properties of Fibers

It has been indicated that stresses along the fiber can develop from horizontal forces acting transverse to the fiber axis as a result of surface friction, shallow cutting, or actual snagging. Since such stresses may cause fiber rupture or slippage in their first occurrence, or after numerous applications, it is desirable to prevent their build-up or at least reduce their magnitude. For a given yarn and fabric, transmission of high stresses along the axes of surface fibers may be reduced markedly by having the fiber yield readily until it can slip under the protuberance of the abradant. In addition, the fiber must return quickly upon release so as to be able to assist in carrying the horizontal load of the abradant surface. Rapid return of the fiber is also essential to protect the underlying fiber from exposure to abrasive action. Hamburger [22, 23] has listed the desirable stress-strain properties of a fiber for maximum abrasion-resistance as follows: low modulus of elasticity; large immediate elastic deflection; high ratio of primary to secondary creep; high magnitude of primary creep; high rate of primary creep. He has further developed energy coefficients of various fibers based on stress-strain performance in tension and related these coefficients to the abrasion-resistance of fabrics and yarns composed of the fibers. Other investigators have stressed the importance of fiber elongation as a requisite to high abrasion-resistance in fabrics [6, 21, 56, 57].

The difference between the elements listed above, which appear to favor fabric surface softness, and the hardness thought to be desirable for minimum damage to a metal surface lies in the inherent assumption that in severe textile wear the abrading surface will possess a much higher order of hardness than the fiber (except perhaps in the case of glass fibers). It therefore becomes desirable for the polymeric surface to give completely with each passage of an abradant particle to prevent the setting-up of critical tensile or shear stresses at local points. Behavior of the surface upon approach of the second and subsequent abradant particles will depend, of course, upon the recovery of the material to its original position and upon its continued motility. On the other hand, where normal service brings the textile in contact with material of an equivalent order of hardness, relative hardness assumes greater significance. Here one observes

TABLE I. TEST OF GLOVE INSERTS WITH VARYING PERCENTAGES OF WOOL AND NYLON [47]

Lot	Type	Without shell		With shell	
		Ave. no. of traversals	Rank	Ave. no. of traversals	Rank
I	75 wool, 25 nylon	27.4	3	83.7	7
II	100 wool, fulled, unbrushed	17.6	7	71.0	9
III	100 wool, shrink-resistant, fulled, unbrushed 56's	9.0	9	71.5	8
IV	100 wool, medium brushed, no shrink-resistance	10.6	8	102.2	4
V	65 wool 56's, 35 nylon, 6-den. fulled, medium brushed, shrink-resistant	20.3	6	83.8	6
VI	65 wool 56's, 35 nylon, 6-den. fulled, medium brushed, untreated	25.7	4	85.4	5
VII	35 wool 56's, 65 nylon, 6-den. fulled, medium brushed, shrink-resistant	43.6	2	105.6	3
VIII	100 nylon, 6-den. fulled, medium brushed, shrink-resistant	56.6	1	108.4	1
IX	100 wool 56's fulled, medium brushed, shrink-resistant	22.0	5	107.0	2

the possibility of reversal of abrasion performance from field to laboratory depending upon the relative hardness of the rubbing surface, or reversals depending upon the type of field use to which the fabric is put. In working with military garments, one must consider the activities of a clerk who sits at a desk the major portion of the day and of a man who spends his time in vigorous fatigue or combat duty. Uniforms provided for varying activities are usually made of different materials, but frequently the same materials are exposed to widely diverse abrading surfaces. Quartermaster test data show that changing of the rubbing surface does not often reverse the abrasion ranking of materials, but it does enlarge or reduce degrees of difference among the materials. An example of this is seen in the data of a test of wool, nylon, and wool-nylon glove inserts [47]. In this case the glove inserts were worn by men engaged in heavy manual labor; in one instance leather shells were worn over the inserts, and in the other the inserts were worn alone. Data shown in Table I demonstrate the general superiority of the nylon-wool and particularly the nylon inserts over the all-wool inserts in the harsh abrasion to which the items were subjected when worn alone. With the same type of action, but restricting the abrasive surface to the inside of the leather shell, little or no difference was noted between certain of the all-wool inserts and the nylon blends.

Reversals in the abrasion-resistance of cotton and wool fabrics have been noted when grey duck, then mineral-dyed duck, was used as the rubbing surface [17]. These same differences were observed even after the waxes, which might have served to invalidate the results, were carefully removed from the fabrics. Similarly, cotton and spun-viscose fabrics have been rated in reverse order of abrasion-resistance when rubbed against card clothing, then against wool [32]. Such reversals are attributed only to differences in abrasives as they affect the test specimen [26, 59] and are not at all surprising in view of similar inconsistencies in measuring the coefficient of friction of several different solids against each other. Generally speaking, then, anomalous data in comparing field and laboratory tests may be expected as a result of differences in the hardness of abradant surfaces; it should be pointed out, however, that such reversals may also occur as a result of changes in other surface properties and conditions of rubbing.

In view of the different speeds with which various fibers will recover from small strains, as evidenced by the differences in liveliness of wool, cotton, rayon, or nylon fabrics, it is to be expected that the relative recovery of the individual fiber between successive blows by abradant protuberances will depend to some degree upon impact frequency, as determined by the spacing of the particles and the speed of rubbing. Herein we see another cause for reversal of abrasion results on a given set of fibers (in fabric form) [59]. An example of this mechanism is manifest in a report of cumulative extension tests [39] on cotton and viscose tire cord where failure was the result of tensile fatigue. In this case, increased speeds of extension reduced the amount of viscous flow and permitted elastic recovery to contribute to the cycle life of the cord. Such information points to the need for the measurement of the fiber properties cited above at the frequencies and the degree of strain to be met in actual fabric wear.

TABLE II. COMBAT COURSE TESTS OF COTTON-NYLON HERRINGBONE TWILL FABRICS [2]

Fiber content (% cotton)		Fabrics Construction Yarn No.		Texture		Average wear score at each cycle stage Trousers				Jackets			
w	f	w	f	w	f	6	12	18	24	6	12	18	24
100 × 100		13	10	84	63	1.5	5.2	8.3	15.1	1.6	6.4	10.5	13.3
100 × 75		13	10	85	65	1.0	3.2	4.9	8.8	4.2	8.3	12.4	17.6
100 × 50		13	10	84	65	1.4	4.0	5.0	9.0	1.9	7.0	10.3	14.1

Discounting the occurrence of isolated reversals in the ranks of the various textile fibers for any of the reasons cited above, one may conclude from the published data that the following order, from highest to lowest abrasion-resistance, applies to the most common fibers [8, 26, 48, 52, 55]: nylon, cotton, wool,* viscose rayon (medium-high tenacity), cuprammonium rayon, viscose rayon (normal tenacity), acetate rayon,† casein.

In one source of the data reported here [52] the ranking was based on both actual wear tests of men's socks and a laboratory index which combined breaking strength and flexing and abrasion performance in both wet and dry states of the fiber. In another case, eight properties were combined in a single index [7]: tensile strength (wet and dry), elasticity, knot strength, elongation, tensile fatigue resistance, flexural endurance, and degree of polymerization. It is of the utmost importance to designate the finish of the fiber being tested, for this factor often holds the key to modified mechanical properties or to surface lubrication [46, 57, 61, 68, 70].

During the war, considerable study was devoted to the relative wear-resistance of numerous fabric constructions, fiber variables, and blends. Interest in the wearing qualities of available commercial fibers, both alone and in blends with other fibers, was directed towards: (1) development of fabrics of improved wear-resistance commensurate with other requirements of weight, warmth, and flexibility; (2) reinforcing the wearing qualities of other fibers whose use may be dictated by economics or other desirable physical requirements; (3) permitting ready substitution of new fibers for currently-used materials in the event of material or production-equipment shortages, without seriously detracting from wear-resistance of the resultant fabric. Although numerous laboratory tests were run to evaluate the wear performance of various fibers, no attempt is made here to report such data. However, where the results of field tests are available, they are included herein since they are the criteria which may be deemed most acceptable in evaluation of a fiber in a general sense for a given end-use.

Consider first the relative durability of cotton fabrics and cotton-nylon blends in a fatigue uniform as evaluated on the combat course (see Table II). The object of this test was to evaluate the utility of including minor percentages of nylon in the filling yarn (12.5% and 25% on weight of the fabric) of sateen fabrics as a means of reinforcing those structural members of the cloth which are subjected to the major abrasive stresses. The data show a significant improvement in the wear life of the cotton trouser for the nylon-cotton blends, although there is no significant difference demonstrated between the two nylon blends of 25% and 50% in the filling. It was thought that the difference between the two nylon blends might have been vitiated by early breakdown of the all-cotton warp, but it was observed in the field test that the filling failed first in 96% of the cases for all three fabrics. A further anomaly is evident in the jacket data, where the nylon blends appear to be equal to or slightly poorer than all-cotton garments. The fact to be derived from these tests is that nylon blends can be used to advantage in extending the wear life of fatigue fabrics in certain garments by inclusion of fairly low percentages of the synthetic polymer based on the weight of the fabric. Further experimentation is warranted, however, to fix the optimum blends for maximum durability depending upon the type of wear to which the garment will be subjected.

The importance of the conditions of abrasion and use of the fabric has been demonstrated in evaluations of the wear-resistance of glove inserts made of wool and wool-nylon blends (Table I). Here it is seen that the nylon serves as a significant reinforcement for the wool when the glove is subjected to the coarse abrasive action of the Camp Lee glove course; but when the abradant is radically altered,

* Also reported as superior to cotton [8].

† Also reported as superior to normal-tenacity viscose rayon [23, 56].

TABLE III. WEAR TESTS OF 15 SERGE FABRICS [51]

Fabric No.	Wt./yd. 56 in. wide (oz.)	Yarn	Texture w	Texture f	Fiber composition	Spinning system	Wear score*
1	16	2/28	70	50	100% wool	worsted	101 ± 11†
2	16	2/32	76	64	100% wool	worsted	141 ± 30
3	20	2/22	68	54	100% wool	worsted	158 ± 19
4	18	2/25	68	54	70% wool, 30% cotton	Merino French worsted	89 ± 11
5	18	2/24	68	54	85% wool, 15% viscose	worsted	157 ± 26
6	18	2/24	68	54	70% wool, 30% viscose	worsted	151 ± 14
7	18	2/28	72	60	70% wool, 30% viscose	worsted	169 ± 12
8	18	2/24	68	54	55% wool, 45% viscose	worsted	188 ± 19
9	18	2/24	68	54	40% wool, 60% viscose	worsted	171 ± 20
10	18	2/24	68	54	40% wool, 60% viscose	cotton	224 ± 20
11	18	2/24	68	54	85% wool, 15% acetate	—	153 ± 15
12	18	2/24	68	54	70% wool, 30% acetate	—	219 ± 20
13	18	2/24	68	54	100% wool (standard)	worsted	139 ± 14
14	18	2/24	68	54	85% wool, 15% acetate	—	149 ± 21
15	18	2/24	68	54	70% wool, 30% acetate	—	183 ± 24

* Based on combat-course wear scores on 8 trousers of each fabric type. (The higher the wear score, the less durable the garment.)

† Standard error of the average wear score calculated by Schiefer [51] using the formula $\sigma_A = \sqrt{\frac{\Sigma d^2}{n(n-1)}}$, where n is the number of traversals of each fabric (*i.e.*, 8) and d is the deviation from the mean.

although all other conditions remain the same, certain of the all-wool materials last as long as the nylon blends.

Considerable research was conducted at the beginning of the war on blends of wool, cotton, and rayon. The object was to evaluate the effect of blends of cotton, viscose rayon, and acetate rayon upon the wearing qualities of 18-oz. serge, the worsted fabric purchased in the greatest quantity during the emergency. The possibility of a wool shortage at that time was real, and every preparation was made for relieving the critical wool shortage with one of several constructions. As it happened, the need to convert was overcome, and the results of the field tests reported in Table III were held in readiness for further emergency changes in specification requirements. The results point to the superior durability of the cotton-wool blend over the all-wool product. However, the loss in other desirable characteristics, such as hand, drape, crease-retention, and crease-resistance, served as a deterrent to the immediate adoption of experimental fabric No. 4. The rayon blends, on the other hand (both viscose and acetate), were shown to affect the wear life of the fabrics significantly, depending upon the percentages of the blend. It was indicated that 15% rayon could be included in the fabric without seriously reducing its wear life or affecting its crease-resistance properties. However, it was deemed inadvisable to include more than 15% rayon from the standpoint of fabric warmth and appearance [51].

Considering again the microscopic detail of fiber breakdown, one becomes aware of the acute lack of reported data on the nature of tensile failure of single filaments. Clegg has shown what a powerful tool the Congo-red staining technique can be in such studies [11]; in her most recent study [12] she has furnished critical evidence of the complex nature of fiber rupture in actual wear. Her observation of numerous fibrous structures points to the importance of fiber cracking and breaking along transverse cracks. Such cracks, contrary to what one might expect, pass freely across fibrils and cell structure without regard to their orientation. Such transverse cracks, occurring in some fibers at intervals of about 20 μ along the entire length of the fiber, have been illustrated for cotton, linen, wool, and silk fibers. The most striking illustration is Clegg's drawing of the cotton fiber stained to show both cuticle and secondary cellulose spirals with 90° transverse cracks cutting across the spiral directions.

From tensile tests on laminar structures, as, for example, a mica specimen with well-defined cleavage planes, one might expect successive failure of the laminas without propagation of cracks. Following

rupture of a surface layer and formation of a small transverse crack, extremely high shear stresses are set up at the apex of the crack, but in the direction of the cleavage planes, as shown by Orowan [43]. As a result, the ruptured surface layer is separated from the next intact layer and peels off the specimen. Thus, in the course of a tensile test several such layers will rupture successively and peel. Similarly, in pure tensile tests of yarn structures where the fibers themselves serve as laminas, one observes a serigraph type of break involving successive ruptures of the most highly strained fibers and a slippage of fibers, but not a splitting or crack propagation across the yarn unless, of course, it is embedded in a rigid matrix. The closest approach to crack propagation in a laminated or cell-structure material is achieved by imposing a nonuniform stress field on the material with the highest stresses at the boundary laminas which are only partially supported by the matrix. Consider, for example, the mica specimen, which requires several hundred pounds force to rupture in a straight tensile test of a thin sheet; if the same specimen is disturbed by the wind in transit to the testing machine it will tear spontaneously. This emphasizes the fact that crack propagation across lamellas can occur only under conditions of a nonuniform stress field, and points to the validity of Clegg's observation that a significant portion of the damage inflicted on the fiber during service is a result of bending and flexing as well as of extension and compression. The occurrence of linearly varying stress intensities, as predicted by elementary beam theory, points to the probability of transverse-crack propagation or splits despite the existence of an axially (or even helically) oriented laminar structure. Clegg has further shown that such transverse cracks occur more often in fibers which are free to move in the fabric structure and which thus suffer only gentle abrasion and surface bruising. It appears that some cracking is initiated by rupture of surface elements through gentle abrasion. On the other hand, filling yarns in tightly woven poplin structures showed many cracks without trace of surface abrasive attrition. These cracks lead to frequent fiber rupture, as evidenced by Clegg's staple diagram of the weft from a poplin shirt (both worn and unused portions).

Fiber Plucking and Fatigue Response

Under conditions of normal wear it is doubtful that the damage evidenced is caused by a single pull of the surface fiber by a passing abradant asperity. The fatigue response of the fiber is most likely involved. If the developed force is initially pure tension along the axis of the fiber, the crimped nature of the yarns and the curvature of the helical path of the fibers in the yarn quickly distort the stress field so that for the case of slight curvature the maximum stress occurs at the outside surface of the bending fiber (from elementary beam theory), while for the case of sharp curvature the maximum stress occurs at the inside surface of the fiber. The latter fact follows from theoretical calculations of stress distribution in thin- and thick-walled cylinders under internal pressure (in this case caused by the cross fibers or yarns) which show the inner surface to be in tension just as in the case of the outer surface.

Our knowledge of the mechanism of fatigue in fibrous high polymers is quite limited. A most complete survey of the entire subject of fatigue phenomena in high polymers has been prepared by Dillon [18]. In addition to discussing research on the limiting cases of static fatigue-rupture, long-term creep, and relaxation under axial loads, Dillon also reviewed the work done on dynamic fatigue of single fibers and of yarns. Few results on dynamic fatigue in tension have been reported for single fibers, but in the case of dynamic bending fatigue the work of Franz and Henning [18], Hermans [25], and Thomson and Traill [64] is notable. Using Franz and Henning's device, Hermans showed bending fatigue to vary with molecular orientation of viscose filaments so that optimum endurance occurred with the orientation caused by 40% elongation of an unoriented fiber. Using a modification of the same device, Thomson and Traill [64] studied the flexing endurance of several fibers; their results are shown in Table IV. As Dillon points out, the results of the test are not strictly comparable since the stresses developed in the fibers will vary with diameter. But the superiority of wool and nylon and the poor performance of the deacetylated cellulose acetate, the casein, and the glass fiber are notable. In fact, there is a striking similarity between the order of abrasion-resistance of various fibers as presented in Table IV and their bending-resistance. This feature may lead one to believe that bending-resistance is, by itself, a reliable measure of the potential abrasion-resistance of a fiber. The answer obviously is that where gentle abrasion and transverse cracks such as are pictured

TABLE IV. FLEXING ENDURANCE OF TEXTILE FIBERS [64]

Fiber	Breaking load (g.)	Diameter (μ)	Ave. no. of bends
Wool	4	24	20,000*
Nylon	6	14	20,000*
Sea Island cotton	4.5	17	3,200
Natural silk	6	15	1,800
Tenasco	6	16	950
Delustra	4	21	660
Boiled-off silk	4	11	370
Soya-bean fiber	3	21	150
Cellulose acetate	4	19	100
Viscose	4	13	75
Casein fiber	3	25	23
Deacetylated cellulose acetate	3	7	1
Glass		8	1

* Some fibers were still unruptured at this point.

by Clegg [12] are the principal mechanisms of fabric breakdown in wear, then bending endurance will play a dominant role in determining fabric performance. Where harsh abrasive action is involved, other physical characteristics than those affecting bending endurance will dominate fabric performance. For example, note the significant increase of abrasion-resistance of the nylon-wool blends in the harsh abrasion tests of wool glove inserts (Table I) or the increase in abrasion-resistance of the cotton-worsted blend over the all-worsted material when tested in the combat course (Table III).

Dillon also describes fatigue studies of tire cords and discusses the effect on fatigue life of the numerous variables of instrument and testing conditions. He indicates that one general law has been repeatedly observed regarding the fatigue life-temperature relationship—namely,

$$\ln L = A - B/T,$$

where L is the fatigue life, T the absolute temperature, and A and B are constants. The relationship has general application to rubbers and fibers, and possibly to plastics, and may be used to calculate activation energies for the fatigue process.

In his discussion of fatigue of bulk plastic Dillon notes that the fatigue fracture of hard plastics appears to be a combination of chemical and purely physical effects, and that the creep process which is governed by laws of molecular flow may be accompanied by formation of tiny internal cracks. Surface glazing and microrupture have been observed in the case of polystyrene, methylmethacrylate, and cellulose acetate held at small strains. The chemical nature of fatigue of rubber has been studied by Tobolsky, who demonstrated the role of oxidative scission in effecting reduced stiffness and lower breaking strength, and the role of cross-linking in producing increased stiffness and brittleness. In the case of glass fibers one can refer to the classical work of Griffith on the effect of ambient gases on the formation and propagation of surface cracks, resulting in the static fatigue which causes glass tumblers to "explode" when left on the pantry shelf.

Dillon's survey emphasizes the need for more quantitative evaluation of the behavior of fibers under conditions of tensile fatigue. Such research should emphasize application of existing theories, such as those of Leaderman and Eyring, to a wider range of materials. With clarification of the significant factors in dynamic fatigue of fibers, it may be possible to separate and so study critically the elements of fabric abrasion which lead to failure through fiber fatigue.

Repeated Flexing of Fabrics

The discussion of this paper has centered on the question of abrasion-resistance, defined as the ability of a material to withstand direct rubbing under conditions of intended use. The detailed mechanism of this form of attrition has been shown to include elements of axial tensile and repeated-bending stresses in addition to elements of frictional wear and surface cutting. Conversely, it can be shown that the flexing of textile materials in the absence of an external foreign abrasive surface can involve elements of internal abrasion between structural members of the fabric as well as elements of axial tensile and repeated-bending stresses. In this case, the abrasion is caused by relative movement of the fibers within the yarns and yarns in the fabric. Relative yarn movement takes place during crimp interchange under application of orthogonal stresses, and during fabric skewing under application of shearing stresses. Relative fiber movement within the yarn takes place as the yarn is bent and the original cylindrical helix of the fiber (in the singles yarn) winds about a uniformly bent cylinder —*i.e.*, a torus. This latter movement is caused by two factors: (1) the build-up of tensile forces on that portion of each fiber which winds around the outer region of the torus, and of compressive forces on that portion which winds around the inner region of the torus; and (2) the change of local helix angle of the fiber as it lies in the yarn. Analytical ex-

pressions for the interfiber and interyarn movements have been developed and will be discussed in a later paper.

It suffices to give an example in which internal wear and flexural stresses are the motivating factors in fabric deterioration—the disintegration of flags and bunting when subjected to severe flexing in a strong wind. If flexural endurance of the fibers were the sole criterion of flag durability, one might expect approximately equal life in nylon and in wool flags. The fact that blends of 75% nylon and 25% wool stand five to ten times the exposure of the all-wool flag before failure occurs emphasizes the significant effect of the internal movement and the axial stresses developed in structural members of the fabric. Which of these latter elements is more important will depend upon the freedom of internal movement as influenced by geometric and frictional factors, for where motility is restricted tensile stresses will be built up locally and vice versa.

Summary

A general mechanism of cloth abrasion has been proposed—one which differs from the process of surface attrition of solid bodies because of the complex geometry of fabric surfaces and the visco-elastic properties of textile fibers. The total mechanism is comprised of three elements, the relative magnitudes of which depend upon the nature of the abradant, the behavior of the fiber in the fabric structure, and the general conditions of rubbing. The three elements of abrasion are: friction, surface cutting, and fiber plucking. Friction and surface cutting cause direct damage to the fiber at local points of contact with abrasive particles. Plucking may cause immediate or dynamic fatigue rupture of the fiber at that point along the fiber length where maximum stress concentration is built up. The horizontal force developed in friction or surface cutting will also develop force components along the fiber axis and thus lead indirectly to tensile or bending rupture which normally results from fiber plucking.

The nature of the frictional phenomenon which takes place when two solids are rubbed together has been discussed. The relationships among forces developed in the cutting of metals has been described, and the utility of photoelastic techniques in the study of surface forces in high polymers has been pointed out. Finally, the forces built up along the fiber axis during fabric abrasion have been considered in the light of the reported dynamic fatigue and flexural endurance of fibrous high polymers. While flexural fatigue and tensile recovery properties form a striking parallel to the general abrasion-resistance of textile fibers, conditions of rubbing have been shown to nullify and even reverse expected differences between the abrasive durabilities of fibers used in experimental cloths.

Thus, it is imperative that the designer of fabric structures consider the nature of the abrasion to which his material will be subjected in actual use. From such consideration he may select his fibers on the basis of their tensile or flexural properties, with a view toward reinforcing the points of potential breakdown in the fabric structure. His second consideration must include the contribution of cloth geometry to the abrasion-resistance of textile fabrics.

This is the first part of the report in which an attempt has been made to develop a general picture of the abrasive mechanism as related to textile materials. It has been found that the Quartermaster experiments on abrasion performance of textiles have helped to form parts of the outline used. Such studies suggest further analysis of particular elements of the theory with a view toward broadening its applicability to all conditions of service. Part III of this report will be devoted to a discussion of these same experiments, with special emphasis given to the importance of yarn and fabric geometry.

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The Improvement of Luster of Cotton

Part I: Measurement of Reflectance Characteristics Related to Luster*

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Abstract

Practical details are given for using two different instruments for measurement of the reflectance aspects of the luster of cotton yarns. Typical reflectance curves for cotton yarns differing in luster because of mercerization are discussed and compared with the reflectance and visual properties of fabrics made from these yarns. The physical measurements on yarns are much better correlated with what the eye sees in the yarns or in the fabrics than are the measurements on these particular fabrics. This indicates that the study of yarns by these methods is useful both for yarn and fabric. In winding the yarns for examination, a cover factor of more than 40 is found to be needed to eliminate the effect of the backing. Other points of technique, such as tension in winding, humidity, and the size of apertures in the optical system, produce small variations which, however, need to be cared for by standardization of technique when small differences in luster are being examined.

SINCE the basis of judgment of luster of cotton in practice is a subjective combination of visual impressions, the central problem of luster measurement is to obtain physical, numerical measurements which correspond to these visual impressions and which can be combined to correlate with the over-all judgment. In a program for improvement of luster it is desirable to have methods which are objective and reproducible and, if possible, which recognize differences as small as or even smaller than those determined by visual judgment. While the problem of obtaining methods which can be demonstrated to have a high degree of correlation with visual judgment and a high power to pick out small differences is by no means completely solved, methods based on measurements of the reflectance in selected directions are objective and are successful in correlating with the larger differences in luster as appraised visually. Such partially successful methods are discussed in this paper, which gives practical details of measuring reflectance characteristics of cotton and presents results on the effect of variations in technique and the level of variability in the material, by which the statistical or physical significance of the measurements can be assessed. The general, wide-scale correlation with visual impression is verified, but more detailed correlations and combinations with other measurements are not undertaken since the primary concern of this paper is the method of applying the optical measurements to cotton materials.

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Instruments and Methods

Instruments

Numerous publications with special reference to textiles [5, 10, 11, 21, 28, 29] have described methods and instruments for measuring luster by means of reflectance. The same kinds of reflectance characteristics are measured to compare the gloss of other materials such as paper, paint and other finishes, and ceramics [16, 17, 19].

In the present work, two instruments have been used—one, a fixed-angle reflectometer; the other, a goniophotometer, or variable-angle photometer in which both the angle of illumination and the angle of view can be varied systematically. These have been described by Hunter [18, 19] so that only a

few practical notes on the specific application to cotton materials are required.

Quantities Measured

Before discussing the use of the instruments, it is logical to review the theoretical definitions of the quantities to be measured. With these in mind, it is then necessary to consider how closely the operational definitions, involving imperfect standards and practical instruments, correspond to the ideal, and whether the discrepancies are of practical significance with regard to measurement of luster in cotton textiles.

The basic quantity measured is directional reflectance. Hunter [19] has defined directional reflectance as "the amount of light reflected in the direction of view, expressed as the fraction of that which would be reflected in the same direction if the perfectly diffusing, ideal white reflector were substituted for the specimen." The perfectly white, ideally diffusing reflector is one for which Lambert's law applies, which may be written [16]:

$$I_r = \frac{cI}{d^2} \cos i \cos r \qquad (1)$$

or

$$I_r = I_o \cos r, \qquad (2)$$

where I_r = intensity of light in the reflected beam at a given point; c = constant defining the whiteness—unity for the ideal white surface or for magnesium oxide standard, lower values for other calibrating standards; I = intensity of incident beam; d = distance from the surface to the point of measurement in the reflected beam; i = angle between incident beam and the normal to the surface; r = angle between reflected beam and the normal to the surface; I_o = intensity of light in the beam along the normal for given conditions of illumination and whiteness.

These relations are diagrammed in Figure 1, which shows the illuminating and viewing beams.

A given pair of angular conditions is defined by the central rays of the beams in any particular measurement of directional reflectance, and is indicated by writing the two angles—for example, 45°, 0° reflectance; 45°, 45° reflectance. These angles are measured from the "normal," a line at right angles to the general surface of the specimen. The complete definition also needs to include the spread of the beams about the central rays [15], but this factor is considered later (p. 478) in examining the effect of experimental arrangements on the results.

The ratio of two directional reflectances is defined as a contrast ratio, and, unless otherwise indicated, is:

$$\text{Contrast ratio} = \frac{45°,\ 45° \text{ reflectance}}{45°,\ 0° \text{ reflectance}}. \qquad (3)$$

This contrast ratio, or "contrast gloss," can be measured directly in the fixed-angle multipurpose instrument. It is sometimes necessary to generalize the idea of contrast ratio to include other combinations of angles, but in this paper, unless otherwise indicated, the term refers to the specific angles in equation (3) and a specific orientation of the yarn—namely, that with the yarns running parallel to the plane of the path of the light.

Variable-Angle Instrument

The variable-angle photometer is the more basic instrument since it can be used to obtain measurements at a wide range of combinations of angles of view and illumination, and at a wide but definite range of conditions of angular spread of the light beams. The standard condition of use in the work described herein has been with viewing at 45° and illumination at a series of angles within the range in which all of the light falls on the specimen. The area illuminated on the specimen varies with the angle, but this increase in total area compensates for the decrease in amount of light per unit area so that the whole series of measurements can be compared without involving a correction for change of angle, as long as angle of view is constant. Most of the measurements are with the viewing and illumination on opposite sides of the normal; however, the in-

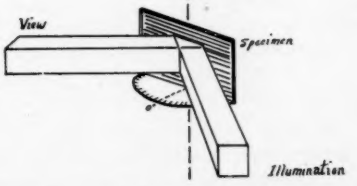

FIG. 1. *Diagram indicating the beams of light. The angle of reflection, or view, and the angle of illumination are each measured between the central line of each beam and the normal (0°), which is at right angles to the general surface of the specimen. The lines drawn on the specimen can represent fibers or yarns arranged parallel to the plane of the path of the light.*

strument permits the two beams to be brought within 22.5° of each other, and measurements with both beams on the same side are useful to show the continuity of reflectance trends.

Fixed-Angle Instrument

The fixed-angle instrument has two directions of viewing—at 45° and along the normal, with illumination at 45°. Hunter [19] has pointed out, following McNicholas [23, 24] and Helmholtz, that angles of view and of illumination are interchangeable, if due regard is given to the cosine factors of equation (1). Thus, 45° viewing, 0° illumination and 45° viewing, 45° illumination in the variable-angle photometer correspond to the conditions in the fixed-angle instrument, since the angles and cosines are the same, although interchanged.

The fixed-angle reflectometer is designed for use in several different ways [18], two of which are of importance in measuring luster characteristics. For measurement of 45°, 0° reflectance, the instrument is calibrated with working standards, usually enamel on steel, which have themselves been standardized in terms of magnesium oxide as 100. In this calibration the 45°, 45° photocell (Hunter's "gloss" cell) is used only to receive an arbitrarily adjusted amount of light diverted from the main beam by a series of mirrors, and does not receive any light directly from the standard surface or from the test specimen which is substituted for the standard at the front of the instrument. The 45°, 0° reflectance is read from the "reflectance" scale.

The fixed-angle instrument can also be used for measurement of contrast properties, although the operations and quantities measured are quite different. The system of mirrors is removed from the light path, by swinging downwards on a hinge, so that both the 45° ("gloss") cell and the 0° ("reflection") cell receive light from a specimen at the front of the instrument. The instrument in this condition will, in principle, directly measure the light reflected along the normal (0°) in terms of that reflected at 45°, using the same reflectance scale as in the other mode of operation, or, using the reciprocal or "gloss" scale, will indicate the ratio of the 45° beam to the 0° beam. This scale thus gives a direct reading of contrast ratio, at least over a certain range, if calibrated by standards of known contrast ratio.

Modification of Fixed-Angle Instrument

In practice, an additional modification of the fixed-angle instrument is required, at least on the models examined, before it can be calibrated to measure contrast ratio. The purpose of this modification is to increase the amount of light received by the 45° cell relative to that received by the movable 0° cell. In principle, this can be accomplished either by putting a neutral filter on the face of the movable 0° cell, or by attaching a bright mirror to the diffusing mirror which is used in calibration to adjust the light received by the 45° cell. The bright-mirror adjustment has been used in all of the present work; it can be easily installed or removed by removing the top of the instrument.

Calibration for Contrast Ratio

For measurement of contrast by this means, it is necessary to calibrate the instrument against a surface for which the reflectance in both directions is known. The enamel-on-steel working standards available for 45°, 0° reflectance are not suitable for 45°, 45° reflectance, in work with cotton textiles, since the enamels are very high in 45°, 45° reflectance, while cotton and other yarns spun from short fibers are relatively low. Fortunately, freshly smoked surfaces of magnesium oxide are primary standards both of 45°, 0° and 45°, 45° reflectance, with ratio unity, and are quite easily prepared as needed. Fairly smooth asbestos board makes a satisfactory base.

Three or more individual magnesium oxide plates should be used to assure calibration. An A.S.T.M. standard method of deposition has been described [7, 8]; the essential feature for the present work is that the coating produced by burning 6 strips of magnesium ribbon, each about 8 in. long, is satisfactory. While it is not difficult to prepare the magnesium oxide standards, the surface chips on contact with the instrument, preventing much re-use. However, the standard method warns against re-use in any event, on account of changes with aging. More convenient working standards of matte vitreous material, such as unglazed ceramic plaques or white structural glass which has been roughened by surface grinding, may be used after calibration. The lowest two members (nominal gloss of 1 or 10) of the series of 60° specular-gloss standards issued by the National Bureau of Standards may be used, bearing in

mind, however, that the calibration supplied is for 60° illumination and viewing, and also on the perfect reflector = 1,000 rather than on the perfect diffuser = 1—that is to say, an additional calibration is required. This calibration can be made by the user, in terms of magnesium oxide and 45°.

Some confusion may be avoided by pointing out that measurements of the amount of light reflected can be expressed in either of two general types of scale. Hunter [19] defines these as: (1) *fractional reflectance,* the fraction of a given incident beam which is reflected by the specimen in the specified direction of view (for example, the N.B.S. gloss standards are calibrated on such a scale × 1,000); and (2) *directional reflectance,* defined previously. While definite numerical relationships connect these scales, as indicated by Hunter [19], the second type, based on the ideal diffuser, is used throughout this paper and in fact in most, if not all, of the papers on luster of textiles. However, it should be noted that if measurements of "specular gloss"—*i.e.,* 45°, 45° reflection—are made in the fixed-angle reflectometer by comparison with a black-glass standard, the results are given as fractional reflectances rather than as directional reflectances, and, although these are proportional to directional reflectances, they are not in the same units.

Preparation and Measurement of Specimens of Fiber

While no data on cotton in fiber form is contained in this report, it may be noted that comparative data can be obtained with these instruments using the method of Adderley [2] to mount the fibers across narrow gaps in cards. It is necessary to use a mask covered with low-reflectance material, such as black cotton velveteen or flock fabric, and to calibrate with the standards behind the mask. With the variable-angle instrument, it is necessary to have either the illuminated area smaller than the masked area at all angles used, or larger at all angles; if the illuminated area is larger, a cosine correction must be used for changing angle of illumination.

Preparation of Specimens of Yarn

Specimens are prepared by winding onto thin, stiff plates. Bookbinder's board, a gray cardboard 0.08 in. thick, has been found satisfactory. The dimensions 3¼ in. × 4 in. were chosen to cover the opening of the fixed-angle reflectometer, and are convenient for symmetrical changes of position, back and front, up and down, when the winding covers the central 3 in. of the 4-in. direction.

A screw-cutting lathe is used for winding. At the usual rate of winding, 64 turns per in., the angle between a yarn and the 3¼-in. edge is 0.14°, and between yarns in successive layers, 0.28°. A more even winding is produced by advancing the yarn more than one yarn diameter each turn than by crowding the yarns. A washboard tension device is used to produce a uniform tension throughout the winding. It is a good precaution to wrap the specimen in paper immediately upon removal from the lathe to avoid oil, dirt, fingermarks, and fiber disturbance.

Specimens of Fabric

The handling and measurement of fabric specimens present no problems, except that the surface must be sufficiently flat and several layers must be used to "cover" the support or backing. A stiff plate behind the fabric is usually sufficient mounting.

Methods of Reporting Results

The results may be reported simply as a table or graph of directional reflectances at a series of angles or at selected angles—usually 45°, 0° and 45°, 45° —or directional reflectances at selected angles may be combined in various ways, as in the contrast ratio defined in equation (3).

Results

Reflectance Characteristics of Cotton Yarn

Before discussing particular points of technique it may be helpful to view the general reflectance characteristics of cotton yarns of varying degrees of luster, as revealed by measurements at a series of angles with the variable-angle instrument. With the general picture in mind, the reflectances at special angles and the contrast ratio can then be regarded as representative of the more complete data.

Measurements have been made for yarns oriented both parallel to and perpendicular to the plane of the path of the light, as defined by the diagrams in Figure 2. For convenience, the first arrangement can be referred to as "parallel," the second, as "perpendicular" or "cross." These two directions differ in the same way that warp and filling do, but the situation with yarns is simplified by having only one

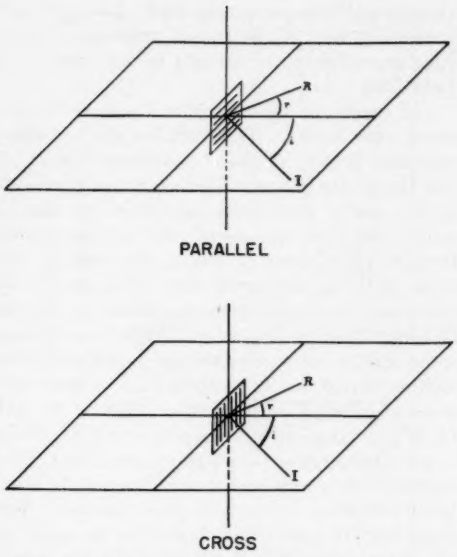

FIG. 2. *Yarns arranged parallel to the plane of the path of the light, as in the upper diagram, are designated "parallel"; yarns arranged perpendicular to the plane of the path of the light, as in the lower diagram, are designated "cross."*

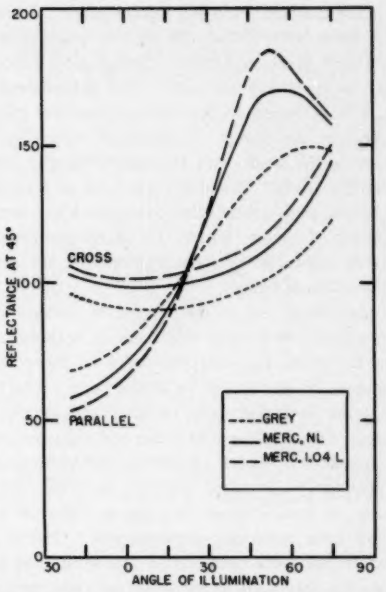

FIG. 3. *Directional reflectances for yarns arranged parallel to the plane of the path of the light (parallel), or perpendicular to this plane (cross). Empire cotton, SRRL Bale 92, 40/2; grey and mercerized at normal length* (NL = *1.00*L) *and at 104%–105% stretch* (*1.04*L).

set at a time, and by elimination of the weaving crimp or bending of one set over and under the other.

Directional-reflectance measurements, all for 45° angle of view but for a series of angles of illumination, are shown in Figure 3 for three cotton yarns.* The properties of the yarns show a clear-cut gradation with increasing application of the processing conditions generally regarded as producing the most luster [22].

For comparison with the curves, and with the discussion of the effects of variations in technique which follows, the values of the reflectances at special angles and the contrast ratios for these yarns are given in Table I. This table shows that the difference between grey yarn and yarn mercerized at natural length is larger than the difference between the two yarns of different conditions of mercerization, whether this is estimated by viewing the whole curves or by considering contrast ratios. The characteristics of the curves of directional reflectance for these yarns are worth noting in some detail, since they illustrate some problems which are encountered repeatedly in interpreting the physical measurements.

Considering first the curves for yarns parallel to the plane of the light, it is to be noted that the yarn mercerized with stretch shows the highest peak; and this peak is sharper and nearer to the 45° mirror angle than is the peak for yarn mercerized at natural length. The peak for the grey yarn is very broad

TABLE I. DATA FOR SPECIAL ANGLES FROM THE RANGE OF ANGLES SHOWN IN FIGURE 1

Material	Arrangement	Directional reflectance (45°, 0°)	Directional reflectance (45°, 45°)	Contrast ratio
Yarn, grey	Parallel	78.5	134.5	1.71
Yarn, merc. *NL*	Parallel	70.5	160.5	2.28
Yarn, merc. 1.04 *L*	Parallel	65.5	175.5	2.68
Yarn, grey	Cross	91.0	98.0	—
Yarn, merc. *NL*	Cross	98.5	108.0	—
Yarn, merc. 1.04 *L*	Cross	101.5	113.0	—

* These materials were supplied by Messrs. Dean and Goldthwait of the Southern Regional Research Laboratory, U. S. D. A.

and is the farthest from the mirror angle. This shift of the peak away from the mirror angle has been commented upon by Quynn, Bernet, and Fischer in recent work on fabrics [28]. For the present purpose, it is sufficient to note as an empirical rule that the higher the luster or gloss of a surface, the sharper is the peak, and the nearer is the peak to the mirror angle. However, the location and broadness of the peak are neither convenient nor sensitive indicators of luster, which, for most purposes, can better be indicated by measurements at 45° and 0°, or by the whole curves.

At the other end of the curves of reflectance for yarns parallel, it is seen that there is nothing unique at the 0° point, but that the order of the curves is the reverse of that at 45° or at the peak. The crossover point does not seem to have any general significance or usefulness in differentiating the yarns. The reversal of order of directional reflectance at 45° and at 0° is rather general, however, in comparisons of textile structures which differ in luster, and has three important consequences. One of these is that the answers obtained by any combined measure of contrast, such as the contrast ratio defined in equation (3), are influenced by changes in both the 45°, 0° and the 45°, 45° reflectances rather than by changes in either alone. A second consequence is that the 45°, 0° reflectance, with yarns parallel, is not a satisfactory measure of general brightness or lightness or whiteness, since it is lower for the more lustrous, "brighter" fabrics. This also applies to other surfaces with distinctly oriented texture, such as fabrics or pads of fiber. This is in contrast to many uses of this measurement for obtaining general brightness or position on the scale from white to black. Thus, the A.S.T.M. standard for directional reflectance of paint finishes [6] states "The combination of illumination at 45° with perpendicular viewing . . . represents a satisfactory average of the directional conditions under which the nonglossy attributes of surface colors are observed in everyday life." The present results are an example, however, of the fact that specimen orientation must be considered in connection with textiles. A third consequence is that wherever this condition of reversal of rank in reflectance with angle is found in physical measurements, it can be seen by the eye, in visual examination, that the relative order of bright and dark changes as the specimens are compared with different conditions of lighting and viewing. Conversely, such changes in viewing lead one to expect a crossing-over of directional reflectance curves. This general rule was brought to our attention by Judd [20].

The curves for yarns oriented crossways may be noted more briefly. The chief features are that a minimum is seen displaced somewhat beyond 0°; that beyond the minimum the curves rise continually as the angle of illumination approaches the glancing angle; and that the general level throughout the three curves is more or less in the order of rank of the peaks of the curves with yarns parallel, but the degree of separation, in magnitude, is more like that near 0° for yarns parallel. While measurements with yarns or fibers perpendicular to the path of the light were regarded as measurements of luster in a series of papers from the Shirley Institute [1, 2, 4, 13, 14], in later papers from this source [3, 5] the luster characteristics have been measured with yarns parallel. The course and general level of the directional reflectance curves with yarns parallel or perpendicular are quite different, and are the source of the contrast effects familiar in damask table "linen," whatever the actual fiber. Here the pattern is formed by warp or filling floats which locally present one or the other condition of yarn orientation.

Even in plain-weave fabric, in which every yarn crosses every other yarn at every opportunity and the "float" length is the minimum, there is contrast between the two orientations of yarn, as well as contrast or high lights along the curved path of the yarns paralleling the line of sight. This local contrast can be seen and appreciated by the observer, but is averaged out in physical measurements of the present type, which view an area which is large compared to the unit of woven structure. By analogy, color measurement on a black and white check would indicate a grey. This averaging effect is reflected in the curves obtained for rather open-structured, plain-weave fabric made from the same yarns, as shown in Figure 4. There is no doubt in an observer's mind that the three fabrics rank as distinctly in order of luster as do the three yarns, but different physical measuring systems than are at present readily available are needed to obtain this correlation at the fabric level.* Of course, these

* A basic difficulty is that the measurements themselves, and the interpretation, regard the specimen as a uniform surface. Several investigators [9, 12, 14, 26, 27] have introduced variations in method or analysis of results in terms of the detailed geometry of textile surfaces which should be developed further.

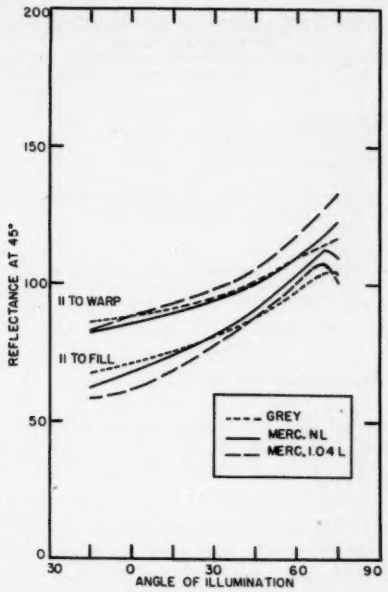

FIG. 4. *Directional reflectances for fabrics made from the yarns of Figure 3. Warp 44, filling 48 threads per in. The curves show the influence of both sets of yarns.*

particular fabrics are probably of the most difficult type for physical measurement; more compact fabrics, and especially twill or satin weaves or less balanced fabrics in which either warp or filling threads predominate in the surface, give better correlation between visual and physical ratings. The most important conclusion from the present comparison is that the properties measured on the yarns correlate strongly with what the eye sees and the mind appreciates in either yarn or fabric.*

Points of Method

Effect of Cover; Number of Layers.—With the screw-cutting lathe one could, in principle, use a setting which would wind the yarns in any of a range of tightnesses of packing per layer and make adjustment for the diameter of the yarn. In practice, a single setting, 64 turns per in., has been found satisfactory for a wide range of yarns. The thickness of cover can be compared in terms of the cover factor:

$$\text{Cover factor} = \frac{n}{\sqrt{N}}, \qquad (4)$$

where n = number of yarns per in. and N = yarn size in cotton count (hanks of 840 yds. in a lb.).

A cover factor of 28 is usually regarded as complete cover for cotton, yarn touching yarn [25]. For 20's cotton count the 64 turns per in. winding gives a cover factor of 14 per layer; for 40's, 10 per layer. Table II shows how the measurements change with number of layers and become stabilized after about 3 layers, or above a cover factor of at least 40. It is not surprising that there should still be a background effect at a cover factor of 28, since the yarns are irregular and are somewhat transparent. A higher minimum cover factor may be required, the more transparent the yarn or the more sensitive the measurements. In another series, using the variable-angle instrument and a finer yarn, the effect of increase in number of layers is not quite complete at cover factor 48, with 4 layers, and indeed is not stabilized until 6 layers, but the results indicate that

TABLE II. EFFECT OF NUMBER OF LAYERS ON MEASUREMENT OF CONTRAST RATIO WITH HUNTER MULTIPURPOSE REFLECTOMETER*

Layers on each side	Cover factor	Contrast ratio: Over glossy Bakelite	Contrast ratio: Over velveteen
1	13.6	2.79	1.99
		2.87	2.04
2	27.3	1.81	1.71
		1.76	1.70
3	40.9	1.61	1.60
		1.59	1.60
4	54.6	1.62	1.62
		1.59	1.57
5	68.2	1.60	1.61
		1.58	1.58

* The yarn used was 22's, 3.9 twist multiplier. Each layer was wound 64 turns to the in. Two kinds of black backing were used—glossy Bakelite and matte black cotton velveteen cemented to a stiff metal plate. The measurements for both sides of the plate are given.

* While the present measurements give chief emphasis to contrast between directional reflectances as the physical basis of the sensation of luster, it should be recognized that other attributes, such as general level of reflectance, maximum brightness in any direction, and transparency or preception of depth, are also involved in the subjective sensation. However, exact definition of these quantities and measurement of their influence are beyond the scope of this paper.

for most comparative purposes 4 layers are sufficient if the backings are uniform.*

Precision of Measurements.—In the regular routine of measurements, the results for the front and back of each plate are averaged. As Table II shows, the two sides are likely to differ by 1% or 2% either in contrast ratio or in directional reflectance. This is a measure both of specimen variability and uncertainty of instrument setting; hence, unless results represent averages for specimens in groups, or a trend of numerous specimens, no attention need be given to differences smaller than about 5%, and results of individual measurements need not be reported to closer than 1%. However, it is useful in a series of directional reflectances with the variable-angle instrument to record the data to the nearest 0.1%, since this represents about the smallest difference which can be observed by the usual technique and shows the trend of a series with a single side of a single specimen, even though the differences between supposedly similar specimens are larger.

In larger-scale comparisons the statistical precision depends, of course, upon the number of independent measurements being averaged and compared, and the statistical probability of observing a given difference by chance (sample fluctuation plus instrument uncertainty) can be calculated from the variability of the data, and serves as a measure of significance.

Effect of Tension in Winding.—The tension during winding can be expected to depend upon the rate of winding and upon the restraint applied to the yarn. A washboard tension device has been used in all of this work; in some work with finer yarns (60's and 80's) a lowering of tension by reduction in the weight pressing the washboards together has been required to reduce the number of breakages, but breaking can usually be eliminated better by control of winding speed. Table III shows that winding speed has only a negligible effect on measurements of contrast ratio, whereas change of tension by change of pressure has a small but definite effect.

Effect of Relative Humidity.—The range of effects of variation in relative humidity are shown in Table IV. These differences are highly significant,

* Further work has shown that it is important that any comparative series be carried out either with constant cover factor and uniform backing materials, or with so high a cover factor that the backing material and depth of layer have no further effect. Cover factors between 90 and 120 may be required to reduce the effect of depth of material to the level of variation along the yarn.

TABLE III. EFFECT OF WINDING CONDITIONS ON CONTRAST RATIO*

	Contrast ratios at tension weights of:			
	24 g.		145 g.	
Speed of winding	(*a*)	(*b*)	(*a*)	(*b*)
Slow (47 r.p.m.)	1.50	1.48	1.54	1.54
Fast (131 r.p.m.)	1.50	1.49	1.53	1.53

* *a* and *b* indicate the two sides of a given plate. The lower tension is used routinely, but speed is varied.

TABLE IV. EFFECT OF RELATIVE HUMIDITY

Condition	Contrast ratio*
65% R.H.	1.68
Dried over $CaCl_2$	1.64

* Averages for 20 specimens.

statistically speaking, being based on triplicate series of measurements by two observers, using 20 specimens; but, in a practical sense, they indicate that conditioning to the standard atmosphere, or a constant relative humidity, is not needed except for the most exacting work, or for year-round comparisons. Frequently, an experimental series is prepared to examine one particular point rather than for general or absolute comparison, and unless the difference produced by the treatment in question is larger than that caused by ordinary fluctuations of relative humidity, it is likely to be of no practical significance.

It is believed that the largest part of the small changes with relative humidity which are observed arise from warping of the backing on which the yarns are wound, owing to differential swelling of the two sides or to differences in moisture effects between backing and yarn. However, this view has not been critically tested, and small effects are to be expected from the swelling of the fibers both as geometrical and mechanical effects and also from any attendant changes in index of refraction.

Effect of Size of Illuminating and Viewing Beams.—In the fixed-angle instrument the measurement of light is accomplished by moving the 0° photocell nearer to or farther from the specimen, using the inverse square law. Hence, the solid angle of view included around the central axis of the 0° beam is continually changing. For high 45°, 45° reflectances there are provisions for neutral filters or smaller openings in the path of the 45° beam, which also change the solid angle of view, in addition to the arbitrary changes involved in the adjustments of initial calibration.

While the sizes of the beams of light or areas viewed in the fixed-angle instrument are difficult to specify, the variable-angle instrument provides for systematic variation. Three general principles determine the choice of apertures:

1. The ideal concept of a parallel narrow beam—in the limit, a single ray—all parts of which are specified as to direction by the central line. The larger the area illuminated, the more the rays from the edge can depart from the direction of the central line and still pass from source to reflecting surface to receiver. This blurring by angular spread of rays will make more difference, the more rapidly the reflection characteristics change with angle—that is to say, the greater the contrast [15].

2. The need to have enough light at the photocell to measure. This may require larger areas of illumination for darker colors, or, when filters are used, to determine the color characteristics of reflection. It also requires larger viewing apertures when smaller source apertures are used in certain ranges.

3. The need, in some series of measurements, to illuminate or view at glancing angles. The illuminated area approaches infinity as the angle approaches 90° from the normal, or 0° from the surface, no matter how narrow the source, but with the variable-angle instrument one can come within 5° of parallel on a specimen extending 3.25 in. in the direction of the spread of the light if one uses a narrowing stop over the source lens. For measurements not going beyond 45°, however, much smaller specimen areas can be used, with economy of time spent in winding as well as in material. Thus, 40 yds. of yarn can constitute a single specimen 2 in. × 1 in. in area on cards 2 in. × 3.25 in.

The working arrangements in the variable-angle instrument are only partially indicated in the diagram in Figure 1. A more complete description has been published by Hunter [19]. However, certain features of the optical arrangements need to be noted here, in order to more closely specify the conditions of illumination and viewing. The beams of light indicated in Figure 1 represent conditions between the front lens of the source and the limiting opening of the receiver. The opening of the receiver restricts the viewing beam to one of four areas which are adjusted to the ratio 1,000:100:10:1. The illuminating beam is slowly converging; the front lens of the source assembly focusses an image of the source slit at the plane of the receiver opening when a mirror is used as specimen or when the two beams are set in a straight line. The angular size of the illuminating beam is specified by the ratio of the width of the source slit to its distance from the front lens. In addition, narrowing stops can be used on the front lens to reduce the portion of the illuminating beam which is used, and these are specified by the ratio of width to distance from specimen. The conditions described so far specify the spread of the beams in the plane of the path of the light; the spread at right angles to this plane can also be specified, but need not be considered further, since its main effect is to vary the amount of light handled in the system.

TABLE V. EFFECT OF CONDITIONS OF ILLUMINATION AND VIEWING

Measuring system →	1	2	3	4	5
Source-slit width	0.2°	0.5°	3°	4°	4°
Source-stop width	2.6°	2.6°	2.6°	2.6°	18°
Receiver-slit width	8.7°	1.3°	1.3°	0.13°	0.13°
	*Contrast ratios**				
Empire cotton, 40/2, grey	1.79	1.83	1.79	1.81	1.79
Empire cotton, 40/2, mercerized	2.50	2.56	2.50	2.60	2.58
Dull filament viscose, 150 den.	2.16	2.24	2.21	2.22	2.17
Semi-dull filament viscose, 150 den.	6.46	7.06	6.70	6.85	6.44
Bright filament viscose, 150 den.	105	120	115	120	117
	Coefficients of variation (%)				
Empire cotton, grey	5.5	1.7	9.7	3.6	1.1
Empire cotton, mercerized	3.2	1.9	4.1	3.7	2.6
Dull filament viscose	5.8	6.4	3.0	8.3	2.5
Semi-dull filament viscose	0.9	0.6	1.0	1.0	0.5
Bright filament viscose	9.6	11.3	8.3	10.0	7.0

* Averages for 10 measurements, 5 on each side, of card *C* of each yarn. System 3 is the one most often used.

TABLE VI. COMPARISON OF INSTRUMENTS

Specimen	Contrast ratio: Fixed angle	Contrast ratio: Variable angle
Various standards		
Magnesium oxide	1.00*	1.02
Roughened white structural glass	1.16	1.16
Ceramic standard, 60° gloss 13.9	2.66	3.58
Yarns (averages of both sides of 2 cards, *A* and *B*)		
Empire cotton, 40/2, grey	1.86	1.78
Empire cotton, 40/2, mercerized	2.56	2.50
Dull spun rayon, 30/1 cotton count	1.40	1.40
Bright spun rayon, 30/1 cotton count	2.27	2.20
Dull filament rayon, 150 den.	1.98	2.28
Semi-dull filament rayon, 150 den.	6.48	6.85
Bright filament rayon, 150 den.	65.5	114
Paper surfaces		
Blotter	1.42	1.40
Manila folder	2.53	4.50
Glazed paper	4.45	24.0

* Fixed-angle instrument is set at this value in calibration.

Table V shows some effects of variation in the width of viewing aperture and of source slit, using a series of yarns covering nearly the whole range of textile luster, from grey cotton to bright filament viscose. Five combinations of viewing and source-slit widths were used, as shown in Table V.

The results show that the measured contrast ratio is more sensitive to change in the width of the receiver beam than to any other one factor. The level of variability, as shown by the coefficient of variation, which is the standard deviation divided by the average, is fairly uniform for all levels of contrast and all combinations of aperture or spread of beam, except that it increases somewhat at the very high contrast of glossy bright filament rayon. These results also show that the differences arising from the departures from the ideal narrow beam or single ray are smaller than the larger differences in luster, such as those between grey and mercerized cotton. However, these operational differences are of a size comparable to differences arising from different degrees of stretch in mercerizing, as shown in Table I, and therefore need to be held constant or accounted for in any series of close comparisons.

Comparison of the Two Instruments.—Measurements on yarns and a variety of other surfaces by the two types of instrument are compared in Table VI. This shows that the results appear to be parallel over a wider range for yarns than for smoother surfaces, such as those of the various standards or of papers. At contrast ratios above 3 for smooth surfaces, or 6 for yarns, the variable-angle instrument with its more narrow conditions of viewing and illumination gives considerably higher contrast ratios. However, the range covered by the fixed-angle instrument is sufficient for most of the work on cotton.

Acknowledgment

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Some Tensile Properties of Wool in Solutions Containing Salt and Acid*

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Introduction

It is generally observed that wool fibers, and many other fibers as well, stretch more easily and retract more completely when swollen. Thus, air-dry wool requires more work for extension than does a wool fiber swollen in water, which, in turn, is more difficult to extend than is a fiber immersed in a dilute solution of hydrochloric acid; the ease of extension parallels the lateral swelling of the fiber in each of these instances. Upon allowing a fiber which had been extended 20% to 30% to retract, temporary set is observed in the usual load-extension curve for the dry wool as contrasted with the complete return to the initial length in the case of the fiber immersed in the aqueous systems. (See, for example, Figures 4 and 5 in [3].) Analogous behavior has been reported for rayon fibers. Thus, it has been shown that rayon fibers swollen in dilute alkali are more readily extended and exhibit more complete recovery than do water-wet fibers [2].

Wool fibers extended while immersed in concentrated neutral salt solutions (*e.g.*, potassium chloride) exhibit the properties of dry fibers, showing large hysteresis work loss and incomplete immediate recovery of length in proportion to the salt concentration. The swelling in such reagents is depressed below that of the fiber in water. The elastic behavior under such conditions is generally explained on the basis of the competition between the wool and the salt for the water, the "atmosphere" of the fiber becoming dryer as the salt concentration increases.

In the course of a study of the felting properties of wool in concentrated salt solutions, some measurements of the stress-strain behavior were made in which small amounts of acid were added to the salt solutions. Instead of improving the recoverability, as might have been expected, the addition of the acid caused the load-extension curves to exhibit an even larger hysteresis between extension and retraction than in the salt solutions alone. The return to the

* This work constitutes a part of the Army Quartermaster program on shrink-resistance of wool for military clothing, which is under the supervision of the National Research Council Committee on Textile Finishing Research.

initial length of the fiber upon retraction was also less complete in the acid-salt mixtures than in the solutions containing salt only. This unexpected finding was considered to be of sufficient interest to warrant further study of the mechanical properties of wool in such media, aside from their connection with felting. The felting of wool in this type of solution will be discussed elsewhere. It is the purpose of the present paper to report observations bearing on the unusual tensile and retractile phenomena in solutions of acid plus salt of the type just mentioned.

Results and Discussion

Clean fibers removed from a commercial wool top of 64's grade were wet-out in distilled water and extended 20% in an autographic fiber extensometer [1] at a rate of 30% per min. After retraction at the same rate, the fibers were relaxed in water, immersed overnight in the solution under study, and then extended to 20% and retracted in the test solution. The fiber could be rinsed, relaxed in water, and then re-run in either water or a third reagent. Data calculated from the load-extension curves of fibers in solutions of salt, acid, and salt plus acid are given in Table I.

The molecular forces opposing extension are presumably also responsible for the retraction of the fiber. The manner in which a fiber recovers from extension depends not only upon the number and magnitude of the intact molecular forces resisting extension but also upon the ease with which molecular segments slip past one another. In reagents which cause the fiber to swell, the increased separation between molecules results in increased molecular mobility.

In 0.1*M* HCl, some of the forces resisting extension must be broken, as indicated by the data for the modulus and work for extension in this solution as compared with those for the fiber in water (see Table I); the tensile force at any given elongation is lower in HCl than in H_2O. It might be supposed that in view of the lowered retractile force, recoverability in HCl would be poorer than in water. However, the swelling and enhanced molecular mobility induced by this reagent overweigh the decreased tensile forces in bringing about complete recovery from extension. In fact, the results in Table I indicate not only complete length recovery but also more complete work recovery in the acid solution than in water.

In solutions which depress the swelling of the fiber, lowered molecular mobility results. The incomplete recovery from extension observed in the 4*M* KCl solution in Table I is a consequence of the high "internal friction" of the molecular chains. The data of Table I also reveal that fibers extended in salt plus acid recover poorly from extension, showing lower work and length recovery than the fibers extended in salt alone. This surprising result is, however, consistent with the observations noted above. In the acidified salt solution, the presence of acid results in the rupture of some of the intermolecular forces as before, irrespective of the presence of the salt; this is indicated by the lower value for modulus and for work for extension in the acid-salt solutions than in the solution containing salt only. The high concen-

TABLE I. MECHANICAL AND SWELLING PROPERTIES OF WOOL FIBERS EXTENDED 20% IN SOLUTIONS OF SALT, ACID, AND SALT PLUS ACID

Reagent	Relative Hookean modulus*	Relative work for extension†	Work recovery‡	Length recovery on retraction (%)	Relative diametral swelling**
H_2O	1.0	1.0	0.47	100	1.0
0.1*M* HCl	.49	.59	.68	100	1.03
4*M* KCl	1.22	1.14	.37	85	.98
4*M* KCl + 0.1*M* HCl	1.04	.89	.34	75	.98
4*M* KCl + 0.01*M* HCl	1.00	.95	.32	78	.97

* The slope of the load-extension curve in the elastic region in the reagent compared to that for water.

† The ratio of the work required to extend the fiber in the reagent to that for extension in water; this is sometimes called the "20% index."

‡ The ratio of the work recovered from extension to that required for extending the fiber; this is sometimes called the "resilience."

** Ratio of diameter in reagent to that in water.

TABLE II. MECHANICAL PROPERTIES OF WOOL FIBERS IN SOLUTIONS CONTAINING SALT AND ACID AT VARIOUS TEMPERATURES

Reagent	Temperature Extension (°C)	Temperature Retraction (°C)	Relative work for extension*	Work recovery†	Length recovery on retraction (%)
4*M* KCl + 0.01*M* HCl	25	25	.95	0.32	78
4*M* KCl + 0.01*M* HCl	40	40	.75	.44	89
4*M* KCl + 0.01*M* HCl	25	40	.94	.36	88

* The ratio of the work required to extend the fiber in the reagent to that for extension in water.
† The ratio of the work recovered from extension to that required for extending the fiber.

tration of salt is, however, still effective in depressing the molecular mobility; this is confirmed by the microscopic measurements of the swelling of the fiber presented in Table I; the relative diameters of the wool in the HCl-KCl solutions are identical with those in KCl alone. The retractile force is thus lower for the fibers stretched in acidified salt solution, while the swelling measurements suggest that the molecular frictional forces approximate those in the neutral salt solution. Hence it is reasonable to expect the rate of recovery of work and length in the acidified salt solution to be lower than in the neutral salt solution.

This view of the mechanism of the extension and recovery behavior in these solutions was tested by additional types of measurements. Elevation of the temperature would be expected to increase the mobility of the molecular segments and thus improve the recovery of work for extension and recovery of initial length in the case of wool in HCl-KCl mixtures. That this occurs is shown by the data in Table II. The last experiment reported in this table (involving a higher temperature of retraction than extension) was performed by adding a sufficient quantity of warm reagent to the solution surrounding the fiber just prior to reversing the extensometer. These results indicate that retraction at higher temperatures does indeed result in recovery of a greater proportion of the work for extension and that fibers so retracted show improved length recovery.

In concentrated lithium bromide solutions in the range from 7 to 10 molar, a considerable number of the secondary forces are ruptured, as indicated by the low values of relative work for extension—about 0.1 to 0.2. Upon recovery from extension the fibers in these solutions show length recovery of only 70% to 80%. It may thus be considered that at high concentrations, lithium bromide combines within itself the dual nature shown by the KCl-HCl mixtures in that both decrease in recoverability and decrease in resistance to extension resulting from secondary-bond breakdown are found. Thus, measurements in these several different types of systems all confirm the strong influence of "internal friction" on the tensile, and particularly the retractile, behavior of the wool fiber.

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Tensile Recovery Behavior of Textile Fibers

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Abstract

The recovery data available on textile materials are scarce and difficult to compare. Very few data on fibers have been presented in which differentiation is made between immediate and delayed recovery. Until the present, no adequate method except the pulse-propagation technique has been known to separate these strain components. Using the Instron tensile tester, a cycling method was developed to measure directly the total elongation and permanent set and to permit also determination of the immediate and delayed recovery. The conditions of the tests were standardized. Some studies were made on the effect of deviations from the standardized conditions.

The recovery behavior of 25 samples representing 16 different textile fibers was measured under the standardized conditions. Their recovery behavior is presented by tabular data and by two series of rectangular graphs. The values of immediate and delayed recovery and of permanent set as obtained describe the recovery behavior of fibers with adequate accuracy from the initial application of stress to the breaking point. The recovery behavior was found to be characteristic for any material; however, it was affected by the history of the samples. The recovery of Fiberglas, cotton, Saran, viscose, acetate, nylon, Orlon acrylic fiber, Fiber V, Vinyon CF-HST, N, NOZZ, NORU, wool, casein, and polyethylene is discussed, and an attempt is made to interpret the data.

Results obtained in this study have been correlated to known recovery data of other authors: Meredith, Maillard and coworkers, and Hamburger.

I. Introduction

This report presents an account of systematic investigations of the stress-strain properties of textile fibers with respect to their recovery behavior.

The stress-strain curve can be used to obtain data on such tensile properties as: breaking tenacity, total elongation at break, the relationship between load and elongation at any given stress or strain value, the yield point or elastic limit, the initial modulus of elasticity (elastic stiffness), and the energy required to rupture (toughness) [34]. Conventional stress-strain curves, however, do not provide information on recovery, an important and fundamental fiber characteristic.

Recovery of stretched fibers is their capacity to return to their original length when extended and then released. Some of the elongation is recoverable immediately, some recovers after a longer time, and some remains permanently. These three components of the total elongation have been termed "immediate elastic recovery," corresponding to perfect elasticity; "delayed recovery," or "primary creep;" and "permanent set," or "secondary creep." Actual as well as relative values of the three elongation components are different in various fibers and are influenced by the stress or strain applied and also by time, temperature, humidity, etc.

Elongation components are related to complex phenomena of textiles which are important from a practical standpoint. Generally, a high level of recoverable elongation is desirable for textile fibers, as are also, in most cases, high tenacity, considerable extensibility, and elastic stiffness. A high proportion of immediate elastic recovery is known to contribute to resilience [7], which, according to Mark [28] and Dillon [15], is a combination of stiffness and fast recovery; to crease-resistance [16] and wrinkle-resistance [18]; to softness of fabrics; to fatigue and wear-resistance; and even to comfort. Cassie [12] emphasized that high accessibility of fiber surface to air is an important factor for warmth of textiles and this is best realized in fibers of high recovery. Delayed recovery is also desirable—however, to a lesser extent. In fact, too high a value may be disadvantageous for special purposes. Delayed recovery frequently causes "relaxation shrink-

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age" in woolen fabrics, creating problems in the tailoring of garments [35]. High permanent set is generally undesirable in textile fibers except in isolated instances. It is known that permanent set can be partly recovered by increasing temperature, humidity, and by permutoid swelling, thus affecting dimensional stability [35]. The value of recovery for a specific use depends on the absolute and relative magnitude of the strain components, and the end-use of a fabric will dictate which of these is of particular interest.

Available data on recovery are sparse, frequently incomplete, and difficult to compare. The best collections of fiber properties—the tables on fibers published in *Industrial and Engineering Chemistry* (1948) [11], *Textile World's* "Synthetic Fiber Table" (1949) [6], and the excellent "Fiber Properties Chart" in *Modern Plastics Encyclopedia* (1950) [38]—contain only a few data on "elastic recovery" or "recovery from strain." Present A.S.T.M. Standards [1] on textile materials do not describe test methods for measuring the recovery of filaments. The German Standard Testing Method provides for the measurement of recoverable and nonrecoverable strain in fibers and yarns [17]; the "degree of elasticity" thus obtained is based on the sum of immediate elastic recovery and delayed recovery. It is common practice in Europe to separate permanent set from recoverable elongation without differentiation between immediate and delayed recovery. Notable contributions to recovery data have been furnished by Meredith [30] in England, and Maillard and coworkers [26, 27] in France. They investigated a wide range of textile fibers using the repeated-cycling technique. Meredith's studies were made on a Cliff-type tester with constant rate of loading using a slight modification of the German Standards. He determined the above-mentioned "degree of elasticity" or "elastic recovery" (ratio of recoverable elongation to total elongation) of many single fibers for different loading steps along the stress-strain curve. Maillard and coworkers used the micro machine of Chevenard at constant rate of elongation for a few single fibers and multifilaments. However, neither of these investigators differentiated between immediate elastic recovery and delayed recovery.

When fibers have been extended and released they are known to recover not only to different extents, but also at different rates of speed. The recovery can therefore be better characterized if differentiation is made between that which is immediate and that which is delayed. The importance of the relationship between recovery and time has been recognized even though no satisfactory experimental method existed for measuring it. Needed information on recovery was obtained first by empirical trials which were subject to individual errors and which proved inadequate for quantitative evaluation. Leaderman [25] investigated thoroughly the time factor in recovery and distinguished between "instantaneous elastic deformation" and "delayed deformation." He also published some data on delayed deformation and on delayed recovery for different fibers using long-duration tests. Hoffman [22] discussed the influence of time and described different kinds of "resilience," also indicating some possibilities for measuring the speed of recovery. Hoffman's four types of "resiliency," represented by such materials as quartz, rubber, wool, and "uncross-linked wool," are based on marked differences in the time necessary for recovery and in the modulus of elasticity. Hamburger [20, 21] emphasized the necessity for determining immediate and delayed recovery separately and quantitatively. Taking advantage of the sonic-modulus technique he used a pulse-propagation meter in connection with the Scott IP-2 constant rate of load testing machine for measuring the deflection components. He determined the "immediate elastic deflection," the "primary creep," and the "secondary creep" of viscose acetate and nylon multifilament on the first loading and unloading cycle and also after repeated stresses. Hamburger's investigation must be considered as the first major step in obtaining comparable data on all three elongation components. The significance of this pioneer work cannot be overlooked.

The tensile behavior of visco-elastic materials is different from the relatively simple performance of such ideal solids as crystalline materials since it is strongly dependent upon the length of time the strains or stresses are applied.

The reason for the differentiation between the three components of the total elongation, especially the separation of immediate and delayed recovery, is mainly a practical one. It is significant to know not only to what extent, but also with what speed, an imposed elongation recovers since some elongated fibers "snap back" and others "creep back" after the tension is released.

Immediate elastic recovery is associated with displacement of atoms or molecules from their positions of equilibrium and with their spontaneous and immediate return when the stretching force is removed. According to present theories, immediate elastic recovery of visco-elastic materials occurs mainly in the amorphous region. This recovery is predominant below the yield point at low stresses and strains. Such recovery is possible when a sufficient number of strong cross-linkages are present to prevent the long-chain molecules from sliding over each other, thus facilitating the return of the deformed structures to their original arrangement. Immediate elastic recovery can also result from the straightening of flexible long-chain molecules or from the unfolding of folded molecules.

Permanent set is a result of the irreversible displacement of molecules, and is associated in visco-elastic materials with one of the following processes: (1) slippage of long-chain molecules, or parts of them, along each other due to the breakdown of the secondary bonds, a process generally accompanied by the formation of cracks and by an opening of the structure; (2) alignment of linear chain molecules by tensile stress, observable in x-ray diffraction patterns and also in electron micrographs of high polymers; (3) stabilization of molecular rearrangements obtained during the stretching process by the formation of new cross-linkages between chain molecules, resulting in a "permanent" elongation which remains after releasing the force since the structural rearrangements attained represent new positions of equilibrium. Permanent set may be present to a limited extent even at extremely low stresses, but it is most easily detected after the elastic limit is exceeded. Slippage and orientation increase with progressively higher strains and they prevail near the breaking point. Although permanent set is irreversible, in general, heat or liquids may remove it, thus causing a shrinkage of the material.

Delayed recovery is best described as a hindered elastic recovery since some displaced molecules continue to return spontaneously for some time after release of the tension. It can thus be considered as an interaction between the mechanism causing immediate elastic recovery and the processes producing permanent set.

Analysis of the total elongation and measurement of the three strain components at any stress or strain value furnish the knowledge necessary for critical evaluation of the inherent tensile properties of fibers. Data of these three strain components characterize without undue complexity the response of fibers to imposed strains and stresses. Meos and coworkers [29] suggested differentiation between five components of the total elongation in a Russian paper dealing with the interpretation of the stress-strain behavior of some typical textile fibers. Measurement of so many components would be too difficult and frequently unnecessary from a practical point of view. In contrast, the present paper describes a method for the measurement of three elongation components using repeated loading and unloading cycles. This technique has been applied in a standardized form to obtain necessary data on the immediate elastic recovery, delayed recovery, and permanent set for a number of fibers.

II. Description of the Technique Used

The elongation components were determined using the Instron tensile tester, Model TT-B * [9]. This versatile apparatus has a weighing system utilizing a bonded-type resistance wire strain gage to motivate the recorder pen. The machine has a wide range of load sensitivities and is operated at a constant rate of elongation (crosshead travel). The moving jaw is mounted on a crosshead which can be driven in either direction at constant speeds to any preselected point. The chart of the recording system is driven synchronously, and therefore its movement is proportional to that of the crosshead. The load-elongation relationship for a test material can be obtained continuously, with a wide variation in load, elongation, and time.

Determination of the three components of total elongation is demonstrated schematically in Figure 1, which was obtained by extending a 100/40/2.5 acetate (No. 16 †) multifilament to 15.5%. This elongation corresponds to 75% of that at break, while the corresponding stress is equal to 90% of the breaking tenacity. To obtain the curve *AM* a specimen of 5 in. (12.7 cm.) gage length was extended first to the selected elongation by moving the pulling jaw of the machine at a rate of 5 in. (12.7 cm.) per min. (*i.e.*, 100% elongation of the speci-

* Manufactured by Instron Engineering Corp., Quincy, Mass.

† The numbers following the samples referred to in this study correspond to those listed in Table II and Figure 7B, in which the characteristics of the samples are shown.

men in 1 min.). The jaw motion was then reversed and the jaw returned to the starting point at the above rate of speed. After this loading and unloading cycle, the specimen was allowed to relax for 5 min. The specimen was then extended again to the same point of elongation in a second loading, *HN*, to measure permanent set. The total elongation is indicated by the distance *AB* for the first loading in Figure 1. The distance *BF* for the recovery curve is equal to *AB*, and the distance *GJ* for second loading is also equal to *AB*. These distances correspond to the preselected 15.5% total elongation. Were it possible to remove the tension imposed in the first cycle at once, or at least at an extremely high speed, the resulting recovery would correspond to the immediate elastic part of the total elongation. As this is not possible with the equipment utilized in the study, it remains to determine the immediate elastic recovery from the recovery curve, *MD*, in the following way: The recovery curve, *MD*, can be considered to have an initial straight portion followed by a more or less curved portion. The length of the linear portion was found to vary widely from material to material and even on the same material when elongated to different degrees. When specimens are unloaded at values below the yield point, the straight portion is large, and relatively small near the breaking point, especially for fibers with high delayed recovery. Figure 2 shows a comparison of the linear portions of the recovery curves for three different materials—polyethylene Type A, Vinyon CF-HST, and Fiberglas (Nos. 25, 15, and 1, respectively)—extended to 31.9%, 17.8%, and 2.1%, corresponding to 63%, 89%, and 91% of their total elongation at break, respectively. These fibers vary widely in their recovery, and also in their extensibility, showing total elongations at break of 50.5%, 20.5%, and 2.3%, respectively. Fiberglas is a very elastic fiber and its immediate elastic recovery is predominant even near the breaking point. The immediate elastic recovery, delayed recovery, and permanent set of Vinyon CF-HST are roughly equal at the elongation shown of 17.8%. Polyethylene A has the highest delayed recovery at the breaking point of all the fibers tested (Table III, column 4, and Table IV, 3a and 3c), and its delayed recovery is predominant at the demonstrated point of 31.9% elongation.

In all cases, the straight portion of the recovery curve indicates a constant relationship between stress and strain corresponding to the Hookean law as a result of the immediate elastic recovery. The deviation from this straight line is caused by the additional delayed recovery. This additional recovery increases during removal of the strain with decreasing stresses and with the time necessary to remove the stress. It thus becomes more marked on the recovery curve as the stretch is removed from the fiber.

The recovery curves of the three samples (Figure 2) reach the line of zero stress after elongations of 21.0%, 9.0%, and 2.0%, respectively, are removed. But these values do not represent the immediately recoverable portion of the total elongation because they contain an additional amount of delayed recovery, which is small for Fiberglas, moderate for Vinyon CF-HST, and large for polyethylene A. Since the recovery curves consist of a straight portion corresponding to the perfect elasticity and an additional curved portion representing the delayed recovery, determination of immediate elastic recovery is possible by extending the linear part of the recovery curve to the line of zero load, thus excluding the delayed recovery. When this is done, the immediate elastic recovery of the three fibers is seen to be 5.0%, 4.3%, and 1.6%, respectively.

The highest practicable jaw speed of the Instron tensile tester was used in these tests to avoid significant errors in the measurement of immediate elastic recovery. Special attention is directed to the inertia of the recording system in the evaluation of the straight portion since it contributes a separate linear part to the curve immediately after reversing the extension. This is easily recognized and is, of course, independent of the material tested; it is disturbing at higher jaw speeds, where an additional limitation occurs through overshooting of the crosshead in reversing its travel. (The complications caused by the inertia of pen response were omitted in the schematic graphs of Figures 1 and 2 in the interest of simplifying the demonstration for a better understanding of the method used.) The jaw speed of 5 in. (12.7 cm.) per min. in these tests represents a compromise between high speed, to eliminate as much delayed recovery as possible, and low speed, to avoid the complications arising from the inertia effect of both the recorder and the crosshead of the Instron tensile tester.

The immediate elastic recovery of the acetate multifilament was obtained similarly in Figure 1 by ex-

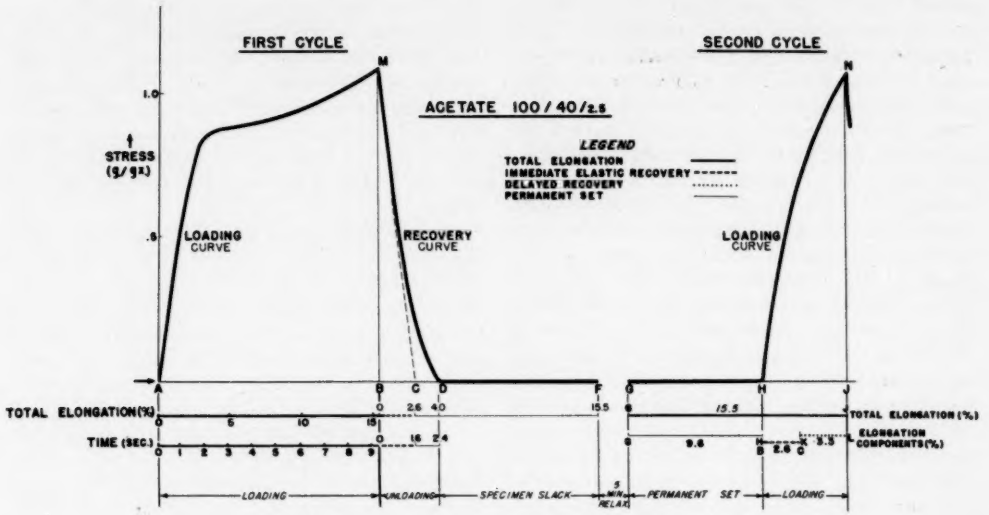


FIG. 1. *Measurement of elongation components.*

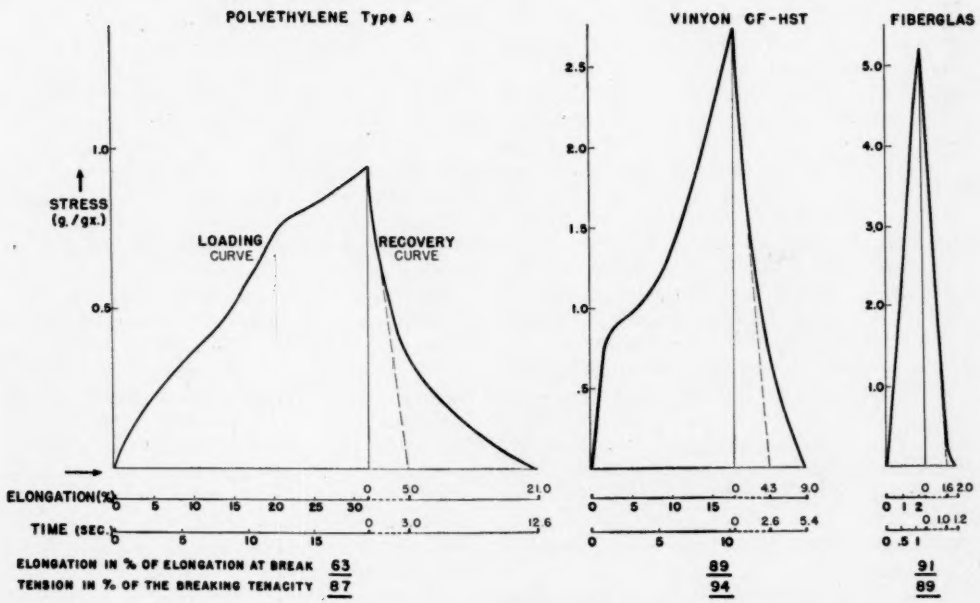


FIG. 2. *Differences in recovery behavior.*

TABLE I. TIME REQUIRED FOR MEASUREMENT OF RECOVERY FOR FIBERS REPORTED IN FIGURES 1 AND 2

1	2	3	4	5	6	7
		Time (sec.) required for:		Immediate	Total elongation:	
Sample No.*	Material	Entire removal of tension	Measurement of immediate elastic recovery	elastic recovery in % of initial length	In % of initial length	In % of elongation at break
25	Polyethylene A	12.6	3.0	5.0	31.9	63
15	Vinyon CF-HST	5.4	2.6	4.3	17.8	89
16	Acetate	2.4	1.6	2.6	15.5	75
1	Fiberglas	1.2	1.0	1.6	2.1	91

* Sample numbers correspond to those in Table II and Figure 7B.

tension of the linear part of the first recovery cycle to the line of zero load to point *C*. It is represented by the distance *BC* on the abscissa, corresponding to a value of 2.6% elongation.

It is admitted that this method has the disadvantages of any extrapolation and is subject to error depending upon individual judgment of the linear part. The four materials demonstrated in Figures 1 and 2 show that the graphical evaluation can be considered fairly accurate for Fiberglas, and good for acetate and Vinyon CF-HST, although somewhat uncertain for polyethylene A. Because of the large amount of delayed recovery, more satisfactory results were obtained on polyethylene A at lower elongations, when the removal of stress can be accomplished in a shorter time. The method used was always accurate below the yield point since immediate elastic recovery is preponderant there and the small elongations applied can be removed quickly. The extrapolation procedure could be questioned since the modulus of elasticity has no constant value at different strains for visco-elastic materials and cannot be represented as a straight line. This behavior may produce a slight distortion of the values obtained, especially at higher elongations, but it is not believed to be significant in most cases. Our data of immediate elastic recovery may be higher than the exact values of perfect elastic recovery; however, they could be measured with greater accuracy, permitting a closer approximation of the exact values, if a much higher jaw speed were used for the recovery.

The time required to measure immediate elastic recovery was in the range of from a fraction of a second to a few seconds in the present tests, and was limited mainly by the response of the Instron tensile tester. This time varied for different fibers and for different elongations of the same material, depending, to a great extent, upon the speed and magnitude of the recovery. Occasionally, it was considerably less than the time necessary to remove tension entirely—*e.g.*, for polyethylene A. The data in columns 3 and 4 of Table I demonstrate the different times for polyethylene A, Vinyon CF-HST, acetate, and Fiberglas at relatively high elongations, as represented in Figures 1 and 2. Columns 5, 6, and 7 in Table I contain further data for comparison. The slight variation in time necessary to measure immediate elastic recovery is not serious in view of the large difference between even the longest time of 3 sec. and the time for measurement of delayed recovery, which was always 300 sec.

There is no doubt that the technique described permits approximation of the true values of immediate elastic recovery despite some minor inadequacies. Its application is fully justified by the present lack of a more practicable method to obtain the quantitative data necessary for the recovery characteristics of fibers, except for the pulse-propagation technique.

In contrast to the determination of the immediate elastic recovery, measurement of the nonrecoverable part of the total elongation is quite simple and conclusive. Permanent set was measured after removing the strain and allowing the sample to recover for 5 min. Indication of stress can be seen on the second loading cycle (Figure 1) only after a definite jaw separation is accomplished at point *H* as a result of increased length of the specimen. Therefore, the horizontal part of this curve, *GH*, represents the part of the total elongation not recovered, or the permanent set, which corresponds to 9.6% for the elongation illustrated. Practical considerations dictated selection of the relatively short time of 5 min. for recovery, although measurements of the permanent set might be more desirable after a longer period of recovery, such as 1 hr., or even 1 day. These values would, of course, be lower than those

reported in this paper, but some would not represent the ultimate values since recovery is incomplete even after many hours.

Direct measurement of the delayed recovery is not easily carried out. Calculations can be made readily from the values obtained for total elongation, immediate elastic recovery, and permanent set. By definition, the total elongation (T.E.) is the sum of immediate elastic recovery (I.E.R.), delayed recovery (D.R.), and permanent set (P.S.):

$$\text{T.E.} = \text{I.E.R.} + \text{D.R.} + \text{P.S.}$$

The delayed recovery is therefore obtainable by subtracting the two measured components from the total elongation. In Figure 1 delayed recovery is represented by the distance KL, corresponding to 3.3% elongation, since

$$15.5\% - (2.6\% + 9.6\%) = 3.3\%.$$

It is obvious that the data for immediate recovery, delayed recovery, and permanent set obtained by the technique described are dependent upon the conditions of the test. Particular conditions are certainly not essential to secure comparable data so long as they remain the same for all tests and permit measurement in approximate equilibrium. The conditions used in the present tests were standardized on the basis of present practicability; however, they are arbitrary. Other conditions might be more convenient or more desirable in special cases, although the values so obtained would be somewhat different. A lower jaw speed, a delay in releasing the specimen after extension, or a shorter recovery period would decrease the recovery values and increase permanent set. A higher jaw speed would decrease immediate elastic recovery data and increase delayed recovery data. Such changes would also alter the tenacity and the entire stress-strain relationship. Although it might be interesting from a scientific standpoint to obtain information under different test conditions, this was feasible only to a limited degree. In a few instances the test conditions were changed to determine the effect on the data obtained; these changes are described on p. 493.

The measurements, as illustrated by Figure 1, must be repeated at various elongations for any material in order to determine its recovery characteristic at a number of points along the stress-strain curve. Generally, between 10 and 20 different elongations were selected for each fiber at scattered points depending upon its stress-strain behavior. The three strain components were measured or computed from this set of curves for each elongation as indicated. These values were then correlated to the maximal stresses of the first loading cycle, which were expressed according to the recommended practice of the A.S.T.M. in g. per grex [2, 33] on the basis of initial fiber fineness. The grex unit of fineness (weight in g. of 10,000 m.) has many advantages compared to the denier unit (weight in g. of 9,000 m.), which is more commonly used for textiles.* Therefore, such an eminent authority as Smith, in his well-known Edgar Marburg Lecture (1944) [34], strongly recommended that the grex system "be adopted immediately by *all* branches of the textile industry."

There are two procedures for testing the recovery behavior from the initial application of strain up to the breaking point. The first consists of extending a single specimen in successive steps along the curve, starting with the lowest point of elongation practicable, and the second involves the use of a new specimen at each selected point of elongation.

The first method was prescribed by the German Standards [17] and it was practiced by Meredith [30] and Maillard and coworkers [26, 27]. Both methods were investigated early in these studies using acetate multifilaments (No. 16). The results obtained by the two methods were found to be essentially the same. They are demonstrated graphically in Figures 4A, 5A, 5a, and 4B, 5B, 5b, which are described later, on p. 493.

However, it was observed that the method using a single specimen had the following disadvantages: (1) When a single specimen is used, it does not reveal sample variability, which is particularly high in some natural fibers; the use of 10 or 20 specimens allows a closer approach to the average behavior of the material; (2) With a single fiber there is no possibility of returning to lower strain values to obtain supplementary data at points of interest, as the previous stress history of the specimen cannot be eliminated; (3) Fatigue of the single specimen makes measurements near the breaking point difficult and controversial. In view of these

* Tenacity given in g. per grex can be converted into g. per den. by multiplying by 1.11, and, conversely, tenacities in g. per den. multiplied by 0.9 correspond to g. per grex data. Tenacity expressed in g. per grex multiplied by $10d$ gives tensile strength in kg./mm.^{2}, and multiplied by $14{,}223d$ gives tensile strength in p.s.i. (d = density).

disadvantages, a set of new specimens was generally used to determine the recovery behavior of each material. When the specimens were reasonably uniform, it was possible to draw a curve through the somewhat scattered points representing the stresses and total strains in the first loading curve. Where excessive variability occurred, it was necessary to increase the number of specimens tested at each strain value. Although the recorded stress values for a given elongation differed appreciably from one another, only that one was selected for evaluation which did not deviate significantly from the average stress-strain curve, based in most cases on ten individual curves, and the remaining values were discarded. Figure 3 shows this procedure for a wool staple yarn (No. 21) which was extended to 15 different elongations, using 3 specimens for each. From these 45 points only the 15 encircled values next to the average stress-strain curve were used for evaluation. While this procedure was time-consuming, it was considered the only way of securing recovery data representative of the average behavior of an uneven material.

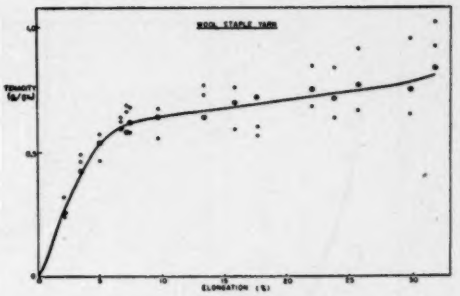


FIG. 3. *Testing procedure for uneven fibers.*

III. Standardized Test Conditions

To obtain comparable and reproducible data on the fibers tested, it was necessary to conduct all tests under the same conditions. The conditions for these recovery tests were standardized as follows:

Gage length	5.0 in. (12.7 cm.)
Rate of elongation	5.0 in. (12.7 cm.) per min.
Removal of elongation	Immediately after extension
Recovery time	5.0 min.
Temperature	70°F (21.1°C)
Relative humidity	65%
Specimens	New fibers for every elongation

IV. Different Methods of Presentation

Typical curves showing the elongation components obtained under the standardized conditions on acetate multifilament 100/40/2.5 (No. 16) are demonstrated in Figure 4A. The tensile stress in g. per grex on the basis of initial fineness is plotted against the total elongation in percent—*i.e.*, increase of length in percent of the initial length. The heavy line is the conventional stress-strain curve, the broken line represents immediate elastic recovery, the dotted line is delayed recovery, and the light line is permanent set. This graph permits determination of the total strain, of that part of the elongation which recovers immediately, of that which recovers in 5 min., and of that which does not recover in 5 min., in percent of initial length at any given stress expressed in g. per grex and at any given strain expressed in percent total elongation. The curves represent average values of the material and were obtained by using 15 different specimens.

The approach of the curves representing total elongation, immediate elastic recovery, and delayed recovery to the zero point was obtained by extrapolation, assuming a linear decrease. The values at the lower elongations (generally less than 2% total elongation, corresponding to an actual elongation of 0.10 in. (0.254 cm.) on the sample tested) are not very accurate and sometimes are considerably scattered. It is difficult to measure such small elongations exactly and to divide them into their components using the described technique. Scattering of points was also frequently observed close to the breaking point. Except for the limitations for these two regions, the reproducibility of the four curves is good when the standard conditions of the tests are carefully observed and the evaluation is made in a uniform manner.

It will be noted in Figure 4A that the total elongation is recoverable below the yield point. Most of the recovery is immediate here and no permanent set appears under the conditions of the test. A marked change in immediate elastic recovery and delayed recovery is noted near the yield point, where considerable increases of strain are accompanied by small increases of stress. The immediate elastic recovery remains nearly constant at higher stresses. The delayed recovery increases rapidly at the yield point until it exceeds the immediate elastic recovery. Above the yield region it does not change appre-

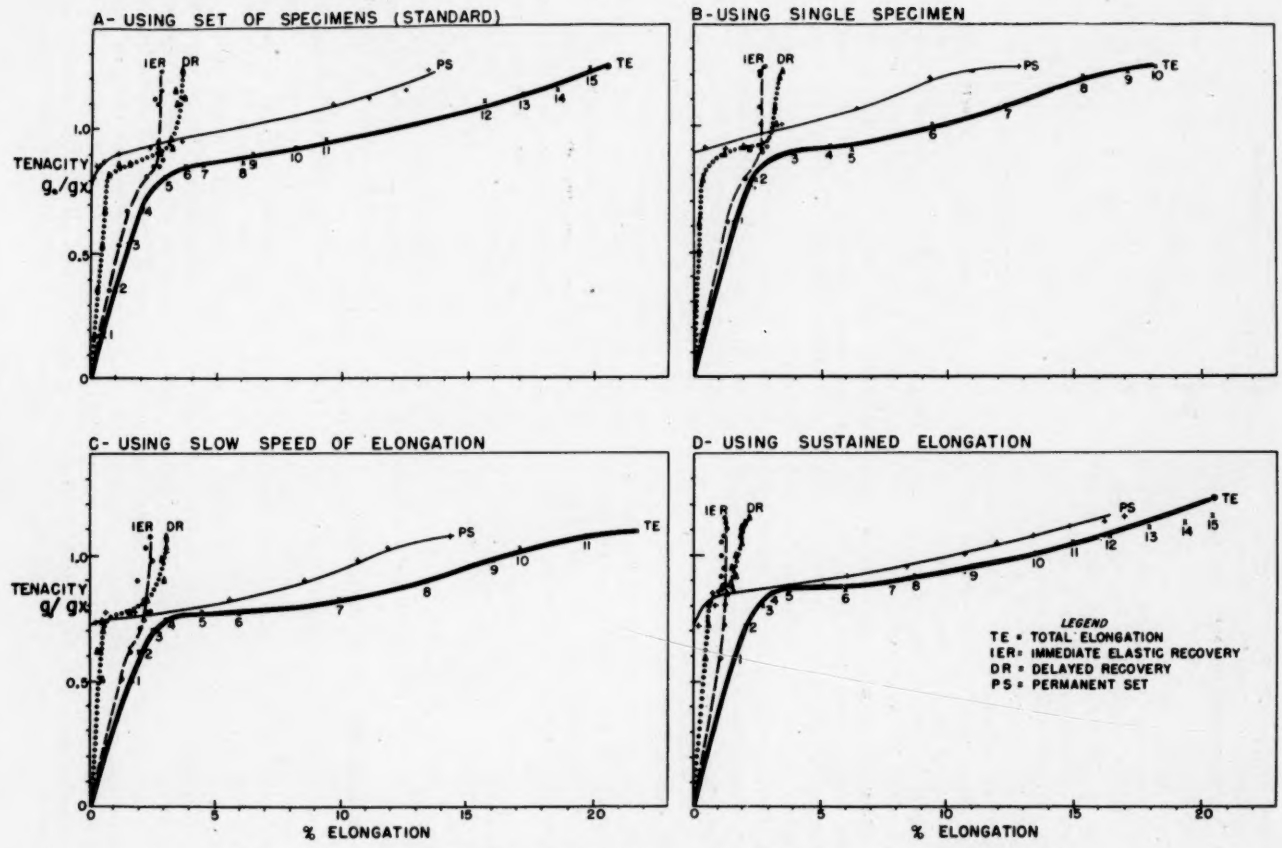


FIG. 4. *Stress-strain curves showing elongation components of acetate multifilament 100/40/2.5.*

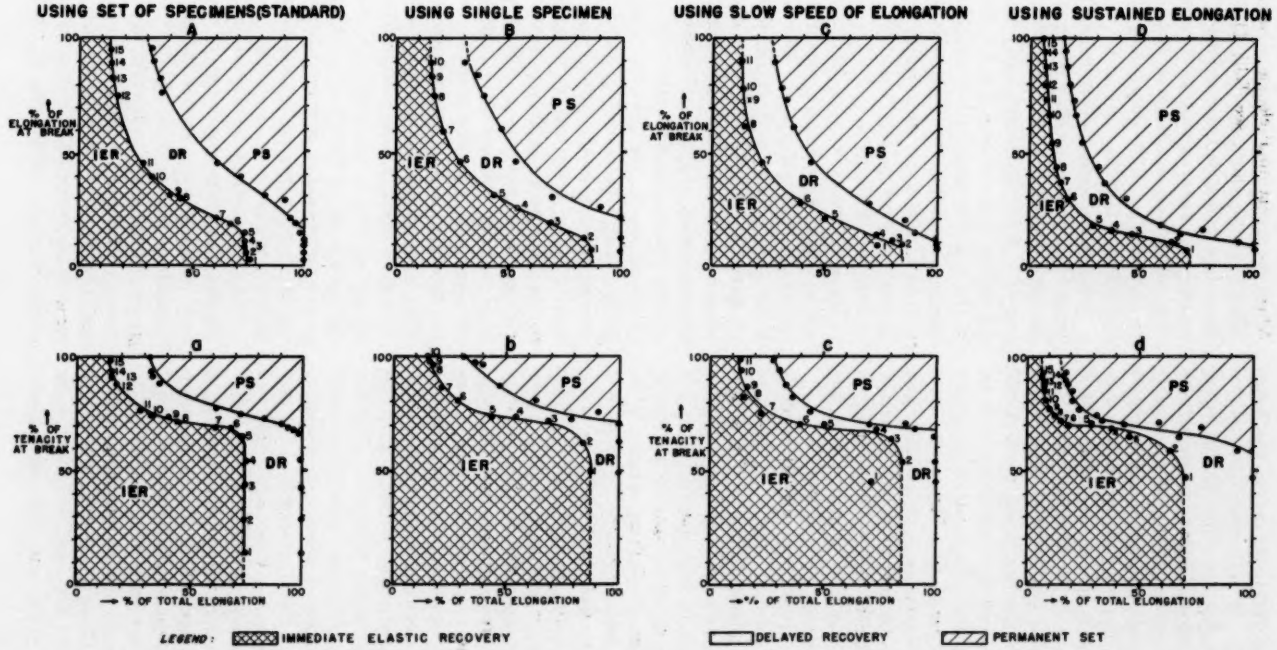


FIG. 5. *Quadratic graphs showing elongation components of acetate multifilament 100/40/2.5.* A, B, C, *and* D *are plotted* vs. *percentage of elongation at break.* a, b, c, *and* d *are plotted* vs. *percentage of tenacity at break.*

ciably. A crossing of these two curves was found in many fibers tested. In such elastic materials as Fiberglas (No. 1) or Fortisan (No. 4), the immediate elastic recovery remains higher than the delayed recovery up to the breaking point, and no crossing of the two curves appears. It is seen also in Figure 4A that permanent set is observable for the first time at the yield point, and it increases markedly and at an almost constant rate to the breaking point.

This general behavior was found for most of the fibers. However, the absolute values of the strain components, their relationship to the stress or strain applied, and their relative values varied in a very wide range, as will be seen later. Figure 4A, showing the four curves, demonstrates clearly the entire stress-strain and recovery performance of the acetate multifilament but is not suitable for the comparison of a large number of textile materials, especially when the properties are decidedly different.

Therefore, another method was selected to demonstrate the results obtained, which are shown in Figures 5A and 5a as quadratic graphs. The elongation components are expressed as percentages of the actual total elongation on both graphs. They are plotted *vs.* percentage of total elongation at break in 5A, and *vs.* percentage of breaking tenacity in 5a. To demonstrate the entire recovery behavior of a material in relation to strain and stress, two separate quadratic graphs are necessary because of the well-known nonlinear relationship between strain and stress in visco-elastic materials. The recovery data for these graphs are calculated from the original values demonstrated in Figure 4A and are reproduced as curves which divide the quadratic field into three parts, representing the elongation components of the material tested as areas from the beginning of stress and strain to rupture. The two quadratic graphs thus demonstrate the three strain components as percentages of actual total elongation at any strain value, expressed as percent of the total elongation at break, or at any stress value, expressed as percent of the breaking tenacity.

For example, Figure 5A shows that at 20% of the total elongation at break, 65% of the actual elongation recovers immediately, 30% recovers after 5 min., and 5% does not recover. At 50% of the total elongation at break the corresponding values for immediate elastic recovery, delayed recovery, and permanent set are 26%, 32%, and 42%; and at the breaking point, 14%, 16%, and 70%, respectively. When the actual total elongation at break is known (20.5% in this case; see Table II, column 8), the percentage values along the ordinate of the quadratic graph can be readily converted to actual values (*e.g.*, 20% of the total elongation at break of this acetate multifilament is 4.1% elongation, 50% is 10.3%, and 100% is 20.5%).

It can be recognized in Figure 5a also that at 80% of the breaking tenacity, 26% of the actual elongation recovers immediately, 32% recovers after 5 min., and 42% does not recover. In comparing Figures 5A and 5a it can be seen that for this sample, 80% of the breaking tenacity is identical to 50% of the elongation at break. It corresponds also to an actual tenacity of 0.98 g. per grex, which is approximately midway between points 11 and 12 on the stress-strain curve of Figure 4A.

The general comments made above in the discussion of Figure 4A are also apparent from both quadratic graphs 5A and 5a. At lower strains and at lower stresses, the predominant part of the total elongation is immediately recoverable and there is no permanent set. The percentage of immediate elastic recovery and delayed recovery is represented at very low stresses and strains by constant values, corresponding to the previous assumption of the linear increase of immediate elastic recovery and delayed recovery in the beginning of the stretching process. The percentage of immediate elastic recovery decreases above the yield point markedly first, and later at a slower rate. The percentage of delayed recovery does not show large variability, and remains nearly the same from the beginning up to the breaking point. The permanent set starts at 15% of the elongation at break and at 68% of the tenacity at break, which corresponds to 3.1% actual elongation, 0.83 g. per grex actual tenacity, and to the yield point in Figure 4A. The nonrecoverable part of the elongation increases steadily with increasing strain or stress and is predominant near the breaking point.

This demonstration by two quadratic graphs showing the elongation components as areas permits an easy comparison of different fibers. The recovery behavior is presented for different fibers, or for a given material tested under different conditions, always by quadrates of the same size, which can be easily compared. However, this demonstration has three disadvantages: (1) it does not show the actual values of strain, stress, and of strain components,

which are often required; (2) it does not show the form of the stress-strain curve which is typical for any fiber; and (3) a classification of different materials on the basis of one characteristic property cannot be easily accomplished. The previous demonstration of recovery data with four curves, as illustrated in Figure 4A, does not have these disadvantages; therefore, both methods have been applied in Figures 4A to 4D, 5A to 5D, and 5a to 5d, respectively, to demonstrate the recovery behavior of the same acetate multifilament observed under slight modification of the test conditions. Comparison and discussion of the final data obtained in this study, however, are not presented either by means of four curves or by two quadratic graphs. Instead, a tabular presentation of numerical data and an illustration by two rectangular graphs for each fiber are used. This demonstration is similar to the quadratic graphs but is free of some of their disadvantages. Both the tabular presentation and the rectangular graphs are described on p. 495 in more detail.

V. Influence of Test Conditions

The results obtained using only one specimen of the acetate multifilament are demonstrated in Figures 4B, 5B, and 5b. Comparison of these graphs with Figures 4A, 5A, and 5a obtained under the standardized conditions demonstrates that recovery data are essentially the same whether a single specimen or a set of 15 specimens is used. Minor differences observed can be attributed to variability within the sample.

Figures 4C, 5C, and 5c illustrate the recovery of the acetate sample when extended at a speed one-tenth of that prescribed by the standardized conditions—*i.e.*, 0.5 in. (1.27 cm.) per min., or 10% elongation of the specimen per min. Figures 4D, 5D, and 5d show the results at the normal speed, where the elongation was sustained for 5 min. at the maximal value of the first loading cycle instead of being released immediately. Both investigations were carried out using a set of samples; thus, only one of the standardized conditions was changed in each case. A comparison of these six graphs with the three graphs obtained under standardized conditions (Figures 4A, 5A, and 5a) shows clearly that the permanent set was somewhat increased when the lower jaw speed was used, and it was considerably increased at sustained extensions. Thus, the recovery in both cases was decreased as expected. These changes are best observable on the quadratic graphs. The general trend of the curves remained, however, the same and no other significant change in the recovery behavior is observable, except for the lower immediate elastic recovery and higher permanent set after sustained elongation in Figures 4D, 5D, and 5d. These changes are results of sustained elongation, which has a similar effect on the fiber properties as does repeated stress or mechanical conditioning.

The graphs discussed above illustrate not only the different methods of demonstration and the extent to which the recovery data can be altered by variation of the test conditions, but they indicate also the applicability of the technique described. Although the recovery values will be changed as a result of modifications in the test conditions, they can be correlated easily to data obtained under standardized conditions when the changes made and their influence on the recovery are known.

VI. Materials Tested

Most of the tests were made on multifilaments of relatively simple construction. It is known that the properties of these yarns correspond in general to those of the base fibers [31].

An attempt was made to conduct all the tests on fiber materials in the same form—namely, 111-grex (100 den.) multifilament with low twist. However, only a limited number of samples were available in this form, many of them deviating in one respect or another. In some cases it was necessary to use single fibers or staple yarns.

It was the goal of this investigation to obtain information on most of the important textile fibers as well as on materials which represent a wide range of properties. The variety of the samples tested is demonstrated best by the 25 stress-strain curves shown in Figure 6. Among the filaments were strong and weak samples; those with high, medium, and low extensibility; natural, regenerated, and synthetic fibers of nearly every type, including the well-known fibers and some relatively new materials.

Many samples are commercially available but a few were experimental. It is recognized that no single specimen of a given fiber material can be taken as representative of all types of that material. The samples were tested as received, without pretreatment to release any strains developed during the manufacturing process.

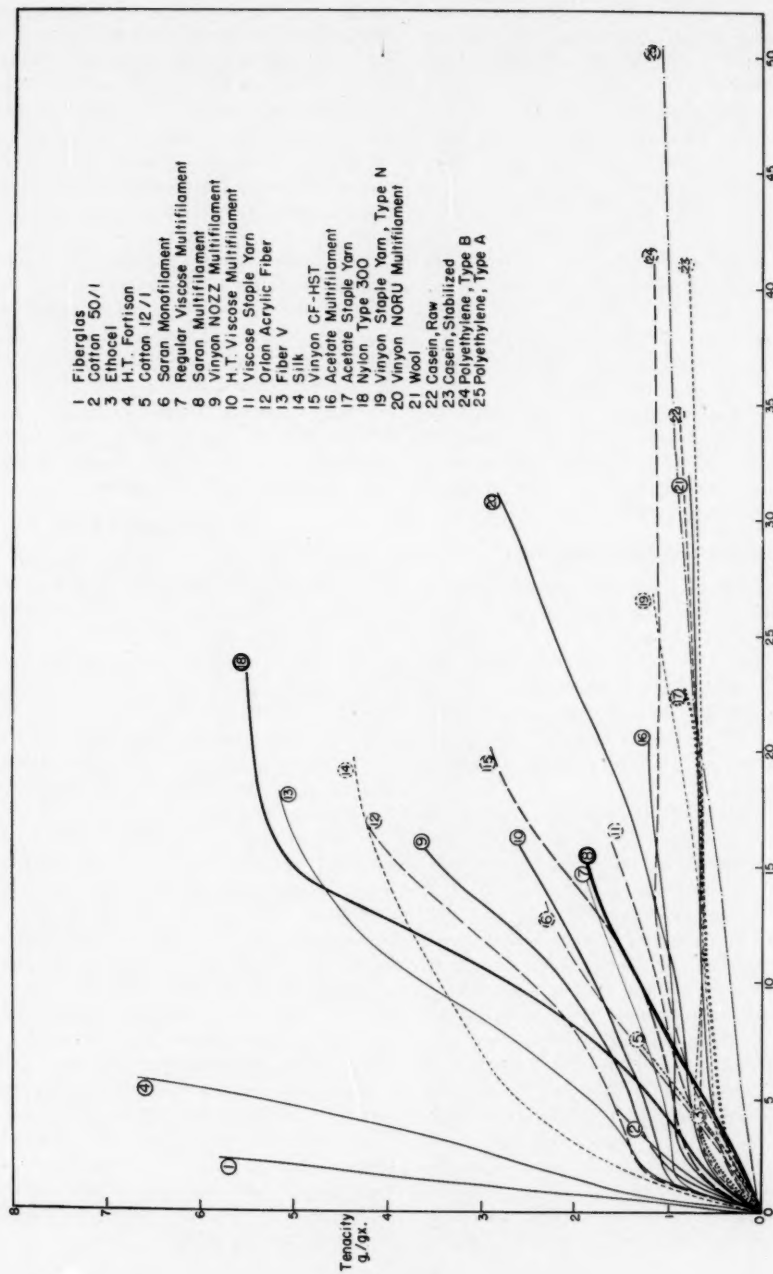


FIG. 6. *Stress-strain curves of fibers tested.*

VII. Presentation of Recovery Data

A tabular presentation of numerical data is the simplest, although not the best, presentation of recovery behavior. Table II shows the fibers tested in order of increasing extensibility, with information on their source, fineness, breaking tenacity, elongation at break, recovery. The list contains 25 individual samples of 16 different materials. The immediate elastic recovery, delayed recovery, and permanent set are expressed as percentages of the actual total elongation at the mid-points of the stress-strain curve (at 50% of the breaking tenacity in column 9 and at 50% of the total elongation at break in column 10) and at the breaking point (column 11). Although the recovery behavior of fibers cannot be characterized fully by numerical values at only three selected points, it is believed that this tabular presentation demonstrates the recovery fairly well for comparative purposes and for general discussion. A few of the values in column 9 are, however, subject to marked errors arising from the uncertainty of measurements at low elongations.

Since it is necessary to know the recovery from the beginning of the stretching up to rupture, the results obtained in this study are also illustrated in Figure 7B by means of two sets of rectangular graphs which represent the entire recovery behavior of the 25 individual samples tested. This demonstration is similar to that illustrated in Figures 5A and 5a by two quadrates, but is free of some of its disadvantages. In both types of graphs data for immediate elastic recovery, delayed recovery, and permanent set are plotted as percentages of the actual total elongation along the abscissa. However, in the rectangular graphs they are plotted against total elongation expressed as percent of original length (in the upper set) and against tenacity expressed as grams per grex (in the lower set). The height of the rectangular graphs represents the extensibility in the upper set and the tenacity at break in the lower set. The samples are arranged in order of increasing extensibility, and their numbers correspond to the sample numbers in Table II. Each rectangular graph is divided into three areas, depicting the immediate elastic recovery, delayed recovery, and permanent set, except the two graphs of Saran monofilament (No. 6), where no permanent set was observed.

The recovery behavior of the acetate multifilament, demonstrated by four curves in Figure 4A and by two quadrates in Figures 5A and 5a, is also demonstrated by two rectangular graphs in Figures 7A and 7a. It can be seen directly from Figure 7A that when this filament is extended to 15%, only 18% of this actual elongation recovers immediately, 23% recovers in 5 min., and 59% does not recover. The actual values for immediate elastic recovery, delayed recovery, and permanent set are 2.7%, 3.5%, and 8.8% elongation, respectively, since the actual total elongation here is 15%. The preponderant portion of the elongation is thus nonrecoverable at this point, with the recovery divided almost evenly between immediate and delayed. Similar information is provided at a given stress value in Figure 7a. It shows that at a stress of 0.90 g. per grex, the values for immediate elastic recovery, delayed recovery, and permanent set are 41%, 42%, and 17%, respectively, of the actual total elongation at this stress value. Since the elongation at a stress of 0.90 g. per grex is shown to be 6.4% on the stress-strain curve of the fiber (Figure 4A), the actual values for immediate elastic recovery, delayed recovery, and permanent set are 2.6%, 2.7%, and 1.1%, respectively. This demonstration by rectangular graphs permits immediate determination of the three strain components as percentages of the actual total elongation for any elongation given in percent and for any tensile stress expressed in g. per grex. Also, actual values of the three components can be computed for any stress and strain from these data when the stress-strain curve is known. In addition, the rectangular graphs facilitate comparison and classification of the fibers tested on the basis of their extensibility, as shown in Figure 7B. The rectangular graphs of acetate multifilament (Figures 7A and 7a) appear in reduced form in the upper and lower sets of Figure 7B as No. 16.

Description and discussion of the results obtained will not be restricted to the relative values of recovery as given in Table II and Figure 7B. They will also cover actual values of the elongation components for the convenience of those who prefer such data.

VIII. Results

A. General

The extensibility of the fibers tested varies from 2.3% for Fiberglas (No. 1) to 50.5% for polyethylene A (No. 25), and the tenacity varies from 0.66 g. per grex for Ethocel (No. 3) to 6.68 g. per

TABLE II. DATA ON TENSILE PROPERTIES AND

1	2	3	4	5	6	7	8
Sample No.	Material	Source*	Characteristic and designation	Remarks†	Actual fineness (grex)	Breaking tenacity (g./grex)	Total elongation at break (%)
1	Fiberglas ECD	1	Multifilament 900-1/2		114	5.81	2.3
2	Cotton	2	Staple yarn 50/1	1	118	1.56	4.6
3	Ethocel	3	Multifilament 500/100/0	2	642	0.66	5.0
4	High-tenacity Fortisan	4	Multifilament 90/120/3		100	6.68	5.8
5	Cotton		Staple yarn 12/1	3	585	1.37	7.9
6	Saran	5	Monofilament 5 mils diam.	4	209	2.32	13.4
7	Regular viscose	6	Multifilament 100/40		111	1.89	14.7
8	Saran	5	Multifilament 200/12/5z	4	222	1.91	15.5
9	Vinyon NOZZ	7	Multifilament 80/40/5z	5, 6	89	3.60	15.7
10	High-tenacity viscose	6	Multifilament 100/40		111	2.51	15.8
11	Viscose		Staple yarn 20/1	7	296	1.61	16.0
12	Orlon acyrlic fiber	8	Multifilament 100/40/z	2, 8	111	4.19	16.6
13	Fiber V	8	Multifilament 100/40	2, 9	111	5.17	18.2
14	Silk	9	Multifilament 100/132		117	4.39	19.9
15	Vinyon CF-HST	6	Multifilament 80/108/3.5	10	89	2.90	20.0
16	Acetate	8	Multifilament 100/40/2.5		111	1.23	20.5
17	Acetate		Staple yarn 20/1	11	296	0.85	22.8
18	Nylon, Type 300	8	Multifilament 100/40/2.5s		111	5.52	23.3
19	Vinyon N		Staple yarn 20/1	5, 12	296	1.14	26.8
20	Vinyon NORU	7	Multifilament 100/60	5, 13	111	2.85	31.1
21	Wool	10	Worsted staple yarn 28.4/1	14	314	0.81	31.9
22	Casein, raw	11	Multifilament 300/40	2	333	0.91	34.4
23	Casein, stabilized	11	Multifilament 300/40	2, 15	333	0.83	40.8
24	Polyethylene, Type B	6	Monofilament 12 mils diam.	2, 16	684	1.17	41.3
25	Polyethylene, Type A	6	Monofilament 12 mils diam.	2, 17	684	1.08	50.5

* Source:
1. Owens-Corning Fiberglas Corp., Toledo, Ohio
2. Standard Coosa-Thatcher Co., Chattanooga, Tenn.
3. The Dow Chemical Co., Midland, Mich.
4. Celanese Corp. of America, New York, N. Y.
5. The Saran Yarns Co., Odenton, Md.
6. American Viscose Corp., Marcus Hook, Pa.
7. Carbide & Carbon Chemicals Corp., S. Charleston ,W. Va.
8. E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
9. Belding-Heminway Co., Inc., New York, N. Y.
10. Forstmann Woolen Co., Passaic, N. J.
11. Eastern Regional Research Laboratory, Philadelphia, Pa.

† Remarks:
1. Staple: 1¼ in. (2.86 cm.), 22.7 t.p.i. (8.9 t.p.cm.)
2. Experimental sample
3. Staple: 1$\frac{7}{16}$ in. (2.72 cm.), 11.6 t.p.i. (4.6 t.p.cm.)
4. Polyvinylidene chloride
5. Copolymer of vinyl chloride and acrylonitrile (40%)
6. Oriented stretched 1300%
7. Staple: 2 in. (5.08 cm.), 3.3 grex.
8. Polyacrylonitrile
9. Polyethylene glycol terephthalate
10. Copolymer of vinyl chloride and vinyl acetate (10%)
11. Staple: 1½ in. (3.81 cm.), 3.3 grex
12. Staple: 1½ in. (3.81 cm.), 3.5 grex
13. Oriented stretched 1300%, reacted without tension 135°C
14. Staple: 2.9 in. (7.37 cm.), U. S. 64's, 20.9 t.p.i. (8.2 t.p.cm.)
15. Formaldehyde-treated
16. Cold-drawn not relaxed, highly oriented
17. Cold-drawn and relaxed, medium oriented

grex for high-tenacity Fortisan (No. 4). A comparison of the upper set with the lower set in Figure 7B illustrates the well-known fact that highly extensible fibers have low tenacities in most cases, but that poor extensibility is not always connected with high tenacity. Broadly, the rectangular graphs of the two sets shows some similarity of pattern, although marked differences exist among the fibers tested. The similarity might be considered as a result of their common structure since all of them, except Fiberglas, consist of long-chain molecules. Their common properties make possible their practical use as textile materials in spite of marked differences in chemical composition and structural details.

The rectangular graphs in Figure 7B clearly dem-

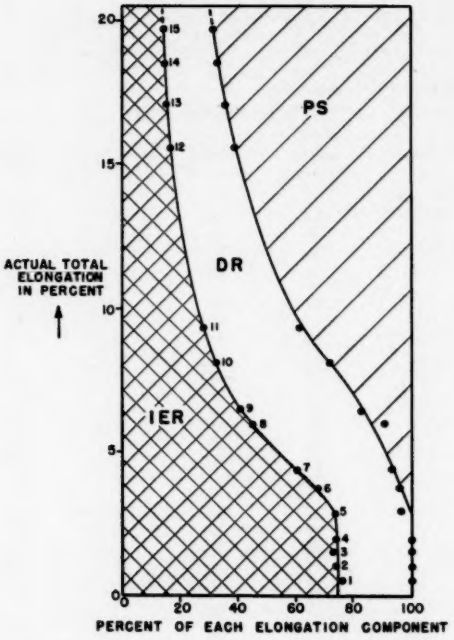
ELONGATION COMPONENTS OF FIBERS TESTED

9			10			11			12
Elongation components in % of actual total elongation:									
At 50% of breaking tenacity			At 50% of elongation at break			At the breaking point			
Immediate elastic recovery	Delayed recovery	Permanent set	Immediate elastic recovery	Delayed recovery	Permanent set	Immediate elastic recovery	Delayed recovery	Permanent set	Sample No.
78	19	3	78	19	3	72	22	6	1
63	35	2	60	34	6	44	32	24	2
71	29	0	80	18	2	50	36	14	3
50	34	16	48	37	15	44	28	28	4
34	44	22	36	46	18	26	30	44	5
53	47	0	53	47	0	42	58	0	6
50	42	8	26	27	47	19	20	61	7
56	44	0	54	46	0	33	54	13	8
39	49	12	40	48	12	26	44	32	9
28	38	34	23	32	45	18	21	61	10
28	32	40	24	30	46	16	22	62	11
30	47	23	30	45	25	21	37	42	12
33	52	15	28	50	22	18	37	45	13
47	42	11	25	33	42	16	20	64	14
27	51	22	30	48	22	25	46	29	15
74	26	0	26	32	42	14	16	70	16
58	42	0	23	25	52	12	18	70	17
29	67	4	27	67	6	18	54	28	18
32	68	0	22	40	38	12	30	58	19
17	39	44	21	41	38	12	28	60	20
64	34	2	28	50	22	16	44	40	21
88	12	0	22	40	38	14	29	57	22
77	23	0	20	30	50	12	28	60	23
76	24	0	22	58	20	10	30	60	24
35	58	7	20	64	16	10	49	41	25

onstrate that recovery at low stresses and strains is complete in every case under the conditions of these tests. The limit for this behavior is about 1% total elongation for Fortisan (No. 4), 2% for viscose (No. 7, 10, 11), 3% for acetate (No. 16), 4% for Vinyon NORU (No. 20), 6% for wool (No. 21), and 11% for polyethylene B (No. 24). This limit corresponds to the yield point where elongation with increasing stress begins to increase rapidly. It is observable on the stress-strain curves as well as on both rectangular graphs, where it is indicated by the beginning of permanent set.

B. Immediate Elastic Recovery

The immediate elastic recovery shows a wide variation at different values of strain and stress for most fibers (Figure 7B). It is always predominant at low elongations and constant values are demonstrated up to the yield point for many fibers according to the previously discussed linear increase of immediate elastic recovery and delayed recovery at very low elongations (Figure 4A). Although this assumption seemed to be justified by the constant relationship between stress and total elongation observable on the conventional stress-strain curves below the yield point, some of the fibers indicated marked deviations from the linearity. Therefore, the validity of our assumption was re-examined on high-tenacity Fortisan (No. 4), acetate multifilament (No. 16), nylon 300 (No. 18), and polyethylene A (No. 25). To obtain more accurate data at low elongations, a longer initial gage length (20.0 in., or 50.8 cm.) was used in these tests. The recovery obtained for Fortisan and acetate indicates a fairly constant relationship between immediate elastic recovery and delayed recovery at the beginning of the stretching process. In contrast to this, a marked increase of immediate elastic recovery at very low stress and strain values was observed for nylon and polyethylene A, as illustrated at the lower parts of the rectangular graphs Nos. 18 and 25. An increase of immediate elastic recovery is demonstrated also



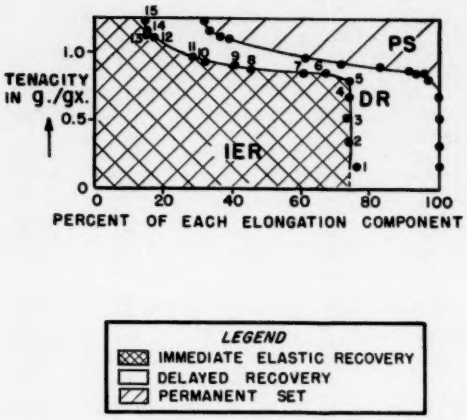


FIG. 7. *Rectangular graphs showing elongation components of acetate multifilament 100/40/2.5.* A—*Left,* a—*Above.*

for Ethocel (No. 3), Fiber V (No. 13), Vinyon CF-HST (No. 15), and polyethylene B (No. 24). Although a few other fibers indicated some deviation from a constant relationship, no definite conclusion was possible from the tests performed as to whether or not the demonstrated constancy in the lower parts of the rectangular graphs should be changed.

The decrease of immediate elastic recovery is nearly linear between the yield point and rupture only for the highly recoverable fibers—Fiberglas (No. 1), 50/1 cotton (No. 2), Ethocel (No. 3), and Saran (Nos. 6 and 8). For all other fibers immediate elastic recovery decreases with increasing strain and stress first rapidly and then at a slower rate. The immediate elastic recovery is usually low near the breaking point, having values between 10% and 40% of the total elongation in most cases (column 11, Table II). It was found higher than 40% only for such elastic fibers as Saran monofilament (No. 6), high-tenacity Fortisan (No. 4), 50/1 cotton (No. 2), Ethocel (No. 3), and Fiberglas (No. 1). It is of interest to note that these high percentages are connected with relatively low extensibilities, which are between 2.3% and 13.4%. The actual values of immediate elastic recovery at the breaking point are in the range of from 1.6% to 5.8% for the fibers tested (Table IV, 3a), but they do not represent necessarily the maximal values for a given fiber. The highest actual values for immediate elastic recovery at the breaking point were found in Saran monofilament (5.8%), Vinyon CF-HST, wool, and polyethylene A (5.0%), Saran multifilament and stabilized casein (4.9%), raw casein (4.8%), and nylon and polyethylene B (4.2%). These fibers can be considered as the most elastic materials tested when only the actual values for immediate elastic recovery at the breaking point are taken into account and the delayed recovery is disregarded.

C. Permanent Set

The permanent set of the samples tested shows even higher variability than the immediate elastic recovery in its actual value, in relation to the total elongation, and in that point at which it becomes observable. Permanent set generally begins at the yield point, and increases steadily and more or less rapidly up to rupture. The start of permanent set may serve as an indication of the limits of stress and strain if the disadvantages of secondary creep are to be avoided. When the recovery data are plotted against tenacity (lower graphs, Figure 7B), a very rapid increase of permanent set is demon-

ERS TESTED

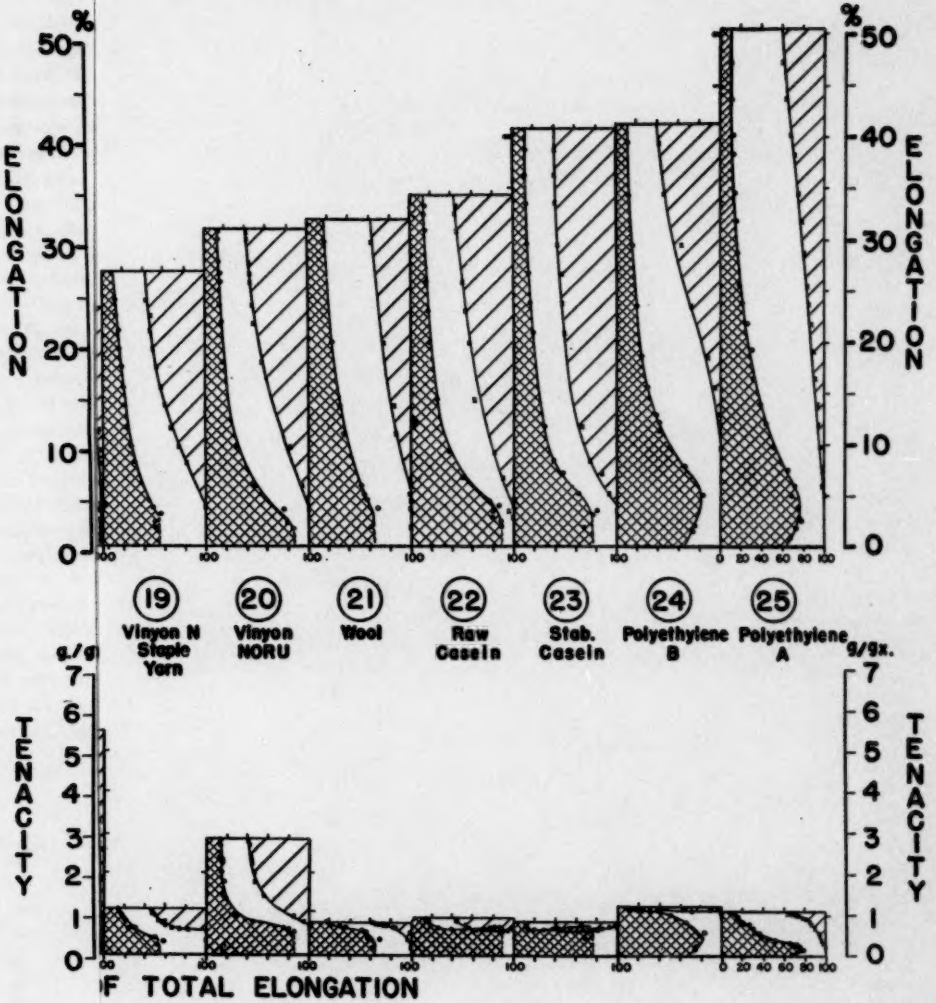
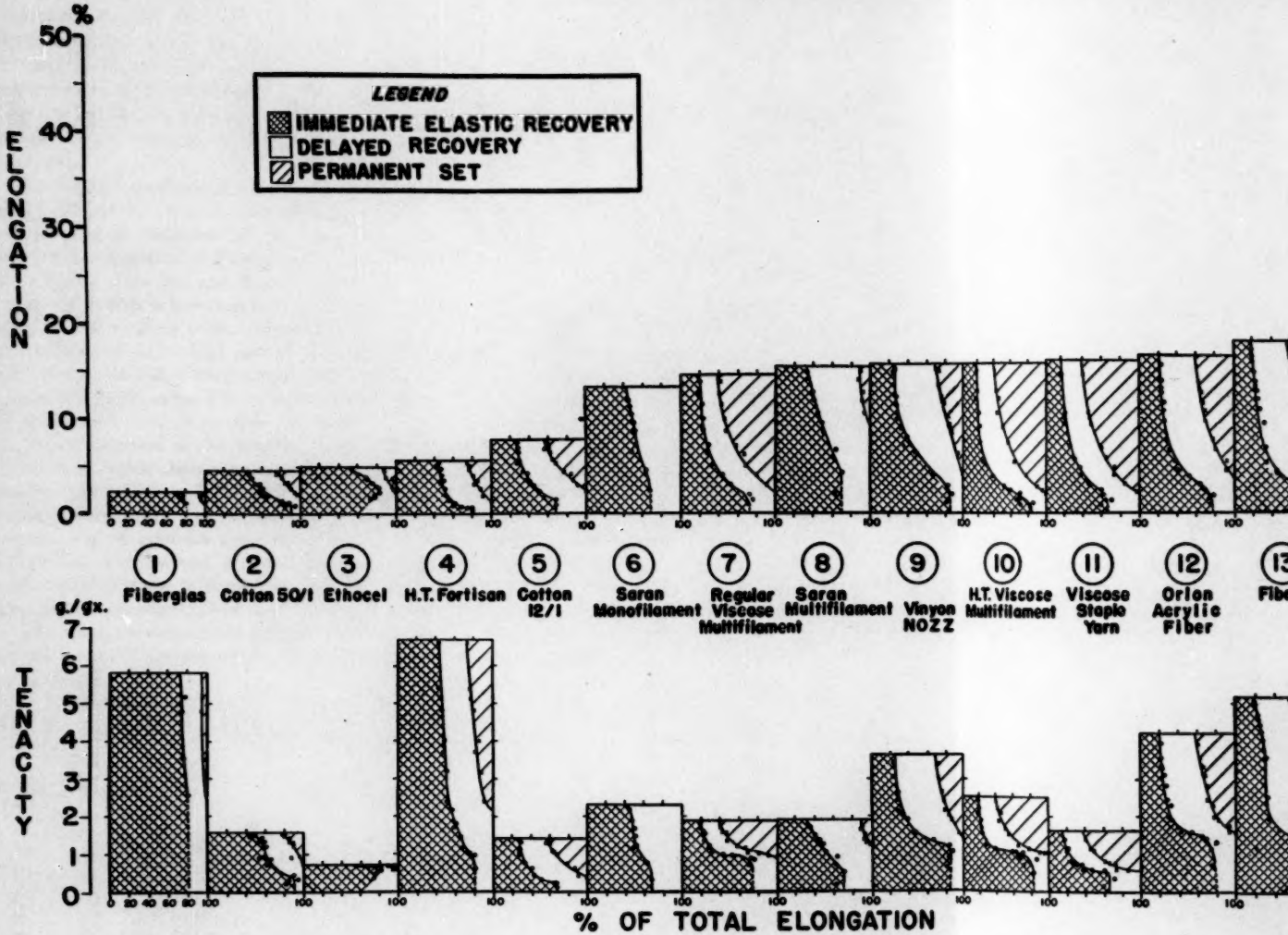
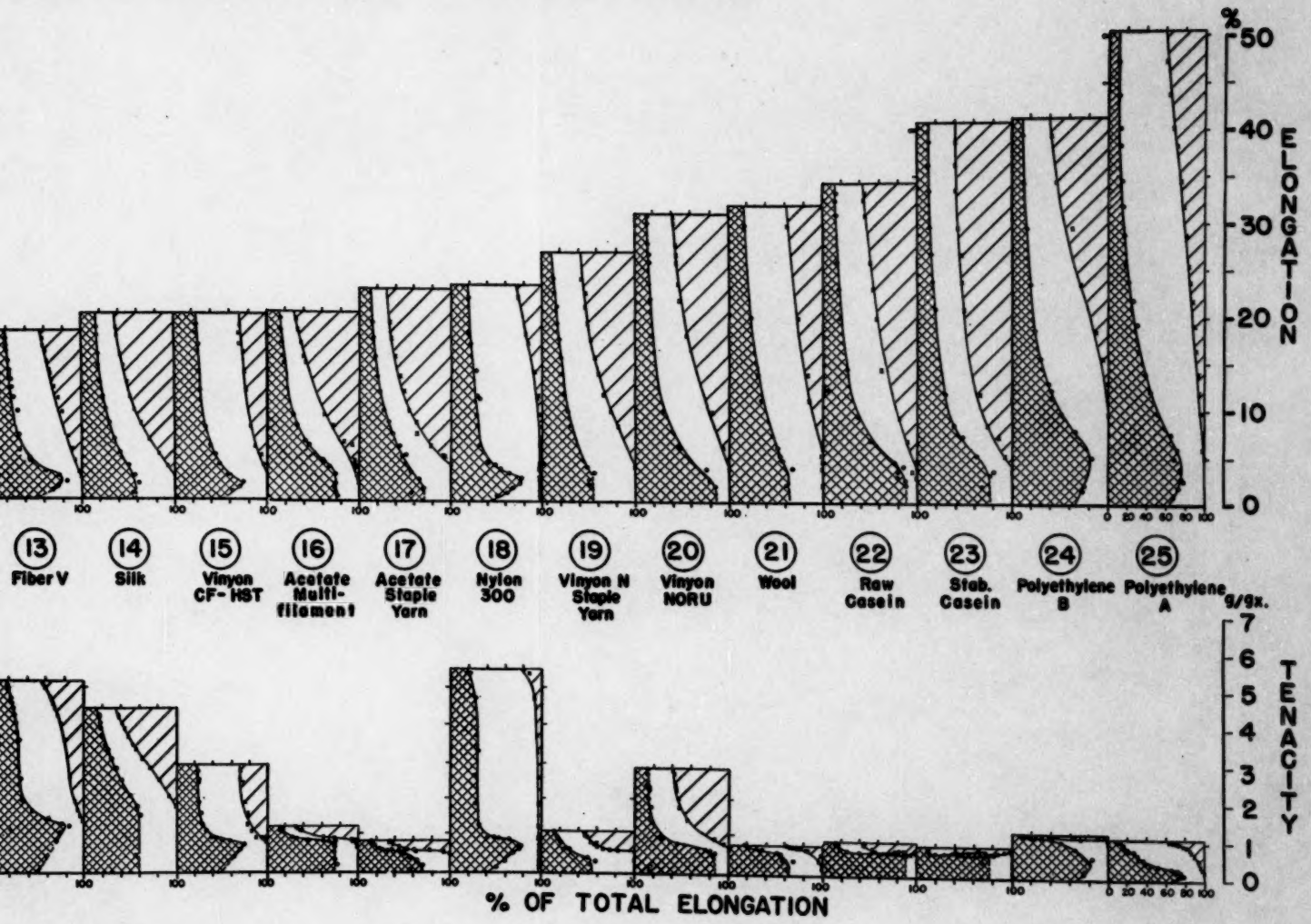
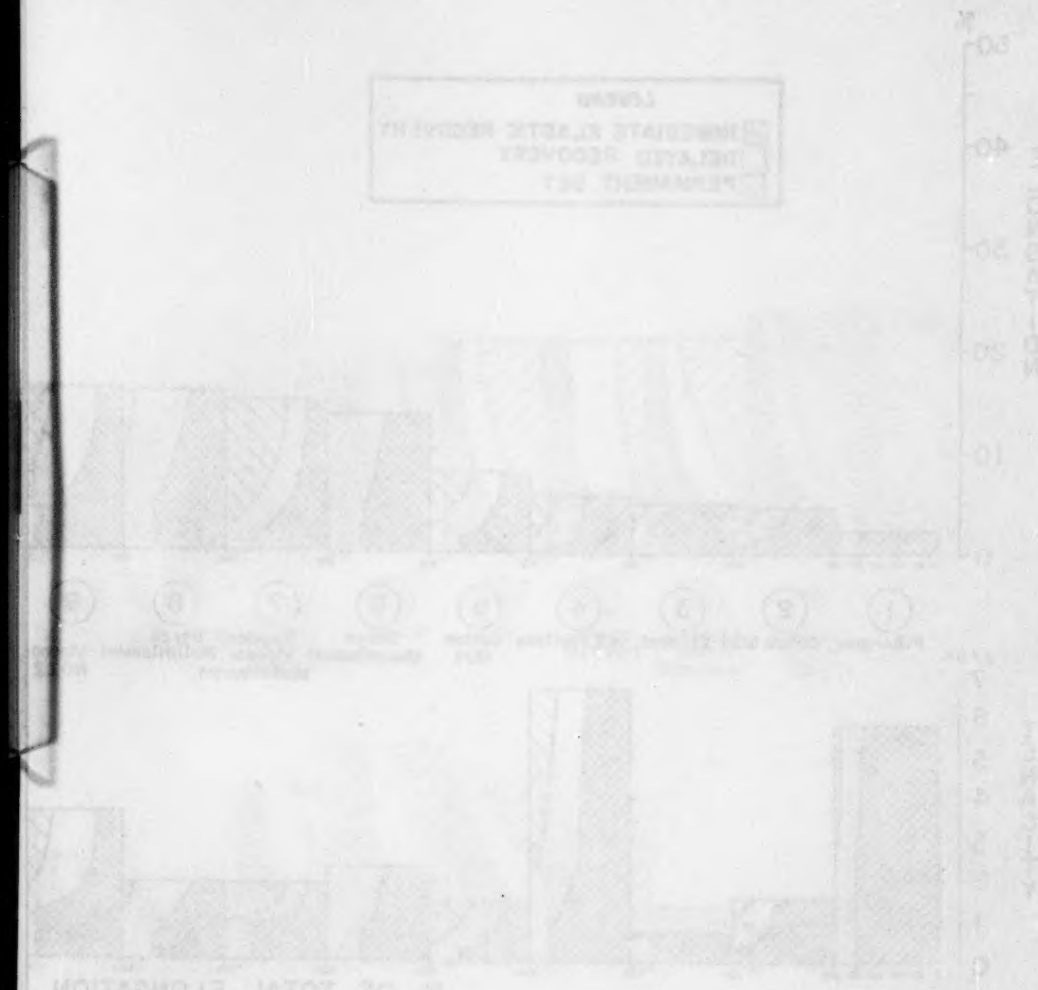

%
ELONGATION
50
40
30
20
10
0
19 Vinyon N Staple Yarn
20 Vinyon NORU
21 Wool
22 Raw Casein
23 Stab. Casein
24 Polyethylene B
25 Polyethylene A
g./g.
TENACITY
7
6
5
4
3
2
1
0
F TOTAL ELONGATION

FIGURE 7B. RECTANGULAR GRAPHS SHOWING



NG RECOVERY BEHAVIOR OF FIBERS TESTED





strated at the yield point for raw and stabilized casein (Nos. 22 and 23) and for polyethylene B (No. 24). The overlapping of the areas for permanent set and immediate elastic recovery in the graphs of the casein samples is due to high plastic flow immediately after the yield point is passed. This is also observable on the conventional stress-strain curves by decreasing tenacities at increasing elongations beyond the yield point. The demonstrated overlapping does not indicate the absence of delayed recovery at any stress values, and can be understood easily by the fact that a given stress corresponds not only to one, but to two or even three different strain values in the critical region near the yield point.

The Saran monofilament (No. 6) was the only fiber evaluated in which no permanent set could be measured under conditions of the test. The nonrecoverable elongation of Fiberglas (No. 1), Saran multifilament (No. 8), and Ethocel (No. 3) is insignificant since it is less than 15% of the total elongation at the breaking point (column 11, Table II). The permanent set of 50/1 and 12/1 cotton, Fortisan, Vinyon NOZZ, Orlon acrylic fiber, Fiber V, Vinyon CF-HST, nylon 300, wool, and polyethylene A is relatively low, in no case exceeding 50% of the total elongation at the breaking point. Many of the fibers tested show a predominance of permanent set (from 50% to 70% of the total elongation) at the breaking point; these include regular and high-tenacity viscose multifilament, viscose staple yarn, silk, acetate multifilament, acetate staple yarn, Vinyon NORU, Vinyon N staple yarn, raw and stabilized casein, and polyethylene B. The actual values of permanent set range from zero for Saran monofilament to 24.8% for polyethylene B at the breaking point (Table IV, 3a).

D. Delayed Recovery

As demonstrated by the rectangular graphs, the percentage of the immediately recoverable and of the nonrecoverable part of the total elongation varies widely from the beginning of extension to the breaking point for any fiber tested. In contrast to this, the percentage of primary creep does not show much variability in Figure 7B and for most fibers it has two distinct values separated from each other near the yield point. These two values remain approximately constant at different stresses and strains, except at the very beginning of the stretching process, where some fibers—*e.g.*, nylon 300 (No. 18) and polyethylene A (No. 25)—show variability in the relationship between immediate elastic recovery and delayed recovery. The percentage of delayed recovery in relation to the total elongation at the breaking point, of course, varies widely from material to material, but still remains between 16% and 58%. It is small (below 25%) for Fiberglas, regular viscose, high-tenacity viscose, viscose staple yarn, natural silk, acetate multifilament and staple yarn; but it is high (above 50%) for Saran monofilament and multifilament and nylon.

The actual values of the delayed recovery at the breaking point are less than 10% for all the fibers tested except for the following highly extensible materials: nylon 300, wool, raw and stabilized casein, and polyethylene A and B. Table III shows actual values of recovery for these 6 fibers, which are listed in order of increasing actual values of permanent set. Beside immediate elastic recovery and delayed recovery, total recovery is also listed (column 5). Total recovery is the sum of immediate elastic recovery and delayed recovery. It corresponds to the recovery data obtained by test methods of the German Standards [17] and to results of other investi-

TABLE III. RECOVERY DATA AT THE BREAKING POINT OF FIBERS WITH HIGH DELAYED RECOVERY

1	2	3	4	5	6	7
Sample No.*	Material	Immediate elastic recovery	Delayed recovery	Total recovery (in % of initial length)	Permanent set	Total elongation
18	Nylon 300	4.2	12.6	16.8	6.5	23.3
21	Wool	5.1	14.0	19.1	12.8	31.9
22	Raw casein	4.8	10.0	14.8	19.6	34.4
25	Polyethylene A	5.1	24.7	29.8	20.7	50.5
24	Polyethylene B	4.2	12.3	16.5	24.8	41.3
23	Stabilized casein	4.9	11.4	16.3	24.5	40.8

* Sample numbers correspond to those in Table II and Figure 7B.

gators who did not separate the two recovery components.

It will be noted that the actual values of immediate elastic recovery in Table III are relatively high, but that those of delayed recovery are markedly higher. The values for immediate elastic recovery, delayed recovery, and total recovery are of the same order of magnitude for the 6 samples, with the exception of the high delayed recovery and high total recovery of polyethylene A. The series can be divided, however, into two groups with respect to permanent set. In the first group are nylon 300 and wool, in which high recovery is accompanied by the desirable property of relatively low permanent set. The second group, consisting of raw and stabilized casein and polyethylene A and B, contains fibers whose high recovery is accompanied by high permanent set, and whose total extensibility is thus considerably increased. Despite their remarkable recovery, these samples cannot be considered extremely elastic (at least not near to rupture) because of their large permanent set values.

E. Range of Recovery Data Observed

The range of tensile properties at the breaking point is shown in Table IV. The data of immediate elastic recovery, delayed recovery, total recovery, and permanent set are presented as actual values (3a) and as relative values (3b and 3c). The relative values of the components are expressed as percentages of the total elongation (3b), corresponding to the presentation in Table II and Figure 7B, and of the total recovery (3c).

It is interesting to compare the small differences in the actual values of immediate elastic recovery (3a, Table IV) with the high variability of the data for delayed recovery, total recovery, and permanent set.

The extremes of the relative values for immediate elastic recovery correlated to total recovery are shown to be 17% and 95% in Table IV, 3c; in most cases, between 25% and 50% of the total recovery is immediate at the breaking point. The high variability of the immediately recoverable portion demonstrates the necessity of separating the total recovery into two components and knowing their relative values for a precise characterization of inherent fiber properties. Although marked differences in the "quality" of recovery (*i.e.*, the speed of recovery) may be observable even by subjective evaluations, it is obvious that smaller differences can be detected only by quantitative measurements of the components.

TABLE IV. EXTREME VALUES OBTAINED ON FIBERS TESTED* FOR TENACITY, EXTENSIBILITY, AND ELONGATION COMPONENTS AT THE BREAKING POINT

	Lowest		Highest	
1. Tenacity (g. per grex)	Ethocel (No. 3)	0.66	Fortisan (No. 4)	6.6
2. Total elongation (%)	Fiberglas (No. 1)	2.3	Polyethylene A (No. 25)	50.5
3. Elongation components				
a. Actual values in % of initial length				
Immediate elastic recovery	Fiberglas (No. 1)	1.6	Saran monofilament (No. 6)	5.8
Delayed recovery	Fiberglas (No. 1)	0.5	Polyethylene A (No. 25)	24.7
Total recovery	Fiberglas (No. 1)	2.1	Polyethylene A (No. 25)	30.5
Permanent set	Saran monofilament (No. 6)	0.0	Polyethylene B (No. 24)	24.8
b. Relative values in % of actual total elongation				
Immediate elastic recovery	Polyethylene A and B (Nos. 24, 25)	10	Fiberglas (No. 1)	72
Delayed recovery	Acetate multifilament (No. 16)	16	Saran monofilament (No. 6)	58
Total recovery	Acetate multifilament (No. 16) and staple yarn (No. 17)	30	Saran monofilament (No. 6)	100
Permanent set	Saran monofilament (No. 6)	0	Acetate multifilament (No. 16) and staple yarn (No. 17)	70
c. Relative values in % of actual total recovery				
Immediate elastic recovery	Polyethylene A (No. 25)	17	Fiberglas (No. 1)	95
Delayed recovery	Fiberglas (No. 1)	5	Polyethylene A (No. 25)	83

* Numbers in parentheses following names of fibers correspond to those given in Table II and Figure 7B.

IX. Discussion of Recovery Behavior of Some Textile Fibers

A. Fiberglas

Fiberglas (No. 1) represents an extreme among the fibers tested. Due to its brittleness, the practical use of Fiberglas as a textile material is limited, despite its high tenacity and its excellent recovery. Its principal limitation is that it is easily damaged in service. The extremely low extensibility and the small amount of permanent set (only 6% of the 2.3% elongation at break) agree well with what one would expect from the atomic structure of silicate glasses, very different from the giant-chain molecular structure of all other textile fibers. According to our present knowledge, silicate glasses are built from a random network of silicon and oxygen atoms. Their arrangement is tetrahedral and the gaps of this structure are filled by the metallic atoms—sodium, potassium, calcium, etc. It is apparent that such a network structure is a strong but very rigid one since no slip planes or long chains are present and no slippage due to breakdown of secondary bonds is possible. Therefore, practically no permanent set is observable as a result of applied strain. The only failure under stress which occurs is rupture of the fibers.

B. Cotton

Comparison of the two cotton staple yarns in Figure 7B shows that the 50/1 yarn (No. 2) has a lower elongation and a slightly higher tenacity than the 12/1 yarn (No. 5). At a given level of strain or stress beyond the yield point, the 50/1 cotton shows a higher recovery than the 12/1 sample. The immediately recoverable part of the 50/1 sample exceeds the delayed recoverable portion, whereas these two components are almost equal in the 12/1 yarn. These differences are also demonstrated by the data of columns 9, 10, and 11 of Table II, where the immediate elastic recovery is seen to be higher and the permanent set lower in the 50/1 yarn than in the 12/1 yarn. For these reasons, the 50/1 yarn can be considered more elastic than the 12/1.

Both yarns were processed from American cotton of similar quality. The cotton fibers and the yarns have the following characteristics:

	50/1 Yarn	12/1 Yarn
Mean staple length (in.)	1$\frac{1}{8}$	1$\frac{1}{16}$
Mean staple length (cm.)	2.86	2.72
Coefficient of length variability (%)	29.4	29.4
Maturity (%)	82	81
Actual fineness (grex)	118	585
Actual fineness (cotton count)	50	10.1
Twist (turns per in.)	22.7	11.6
Twist (turns per cm.)	8.9	4.6
Twist factor: $\frac{\text{turns per in.}}{\sqrt{\text{actual cotton count}}}$	3.21	3.65

The tensile behavior, including the recovery of these staple yarns, is a function of the single fibers as well as of the yarn construction. It is reasonable to assume that their common characteristics, such as low extensibility and tenacity but relatively high recovery, are inherent cotton properties. The recovery is understandable in view of the morphology of the cotton fiber and of the molecular structure of cellulose. Cotton fibers consist of many fibrils, oriented at an acute angle with respect to the fiber axis. In cellulose the lateral forces of attraction between the chain molecules are high due to so-called hydrogen bonds formed by the three hydroxyl groups per anhydroglucose unit. This explains the marked recovery despite the inflexibility of the cellulose molecules. The differences observed between the two yarns might be caused by the differences in fineness and twist factor or by possible processing variations. In any case, the finer 50/1 yarn with the lower twist factor has higher recovery and tenacity but lower extensibility.

C. Saran

The two Saran specimens tested show a behavior similar to the cotton samples. The Saran monofilament (No. 6) has a higher recovery and tenacity but lower extensibility than the Saran multifilament (No. 8). The lower immediate elastic recovery and tenacity, the low permanent set, and, consequently, the somewhat higher extensibility of the multifilament are probably due to a lower orientation, or the presence of plasticizer, or the filament construction.

D. Multifilaments and Staple Yarns of Viscose, Acetate, and Vinyon N

The graphs in Figure 7B and the data in Table II for 3 entirely different samples of viscose (regular and high-tenacity multifilaments and staple yarns,

TABLE V. COMPARISON OF TENSILE PROPERTIES OF ORLON ACRYLIC FIBER, FIBER V, AND NYLON 300 AT THE BREAKING POINT

	Orlon acrylic fiber (No. 12)*	Fiber V (No. 13)*	Nylon 300 (No. 18)*
1. Tenacity (g. per grex)	4.19	5.17	5.52
2. Total elongation (%)	16.6	18.2	23.3
3. Elongation components			
a. Actual values in % of initial length			
Immediate elastic recovery	3.7	3.1	4.2
Delayed recovery	5.9	6.6	12.6
Total recovery	9.6	9.7	16.8
Permanent set	7.0	8.5	6.5
b. Relative values in % of actual total elongation			
Immediate elastic recovery	22	17	18
Delayed recovery	36	36	54
Total recovery	58	53	72
Permanent set	42	47	28
c. Relative values in % of actual total recovery			
Immediate elastic recovery	39	32	25
Delayed recovery	61	68	75

* Numbers correspond to those in Table II and Figure 7B.

Nos. 7, 10, and 11) show a rapid increase of permanent set starting at the yield point and a predominance of permanent set at the breaking point, immediate elastic recovery and delayed recovery being nearly equal. The marked similarity in the relative magnitudes and in the actual values of the elongation components for the 3 samples is evidence that the recovery behavior obtained in this study is characteristic for viscose and is fairly independent of the structure of the samples tested. Differences in values (column 9, Table II) at 50% of the tenacity at break, however, are caused mainly by very rapid changes in this region. This also demonstrates the inadequacy of presentation by numerical data at selected points. It must be admitted, however, that other specimens of viscose whose properties are more markedly affected by significant differences in manufacturing processes or in previous history may exhibit larger differences in recovery than were observed here.

Recovery of the two acetate (Nos. 16 and 17) and Vinyon N (Nos. 19 and 20) samples indicates that the behavior of these materials is similar to the recovery of viscose, despite some differences in breaking tenacities and extensibilities. Acetate shows a higher permanent set at the breaking point than viscose, and delayed recovery is predominant in the recoverable part of the Vinyon N samples at the breaking point. Comparison of the multifilaments with the staple yarns corroborates the observation made on viscose—namely, that the magnitude and shape of the three areas for recovery in the rectangular graphs of the multifilaments and staple yarns are very similar and that corresponding values of recovery in Table II are also in good agreement except when compared at 50% of the tenacity at break.

E. Nyon 300, Orlon Acrylic Fiber, and Fiber V *

Nylon 300 (No. 18), a strong and extensible fiber, is remarkable for its high actual value of total recovery (16.8%) and, consequently, for its low permanent set (6.5%) at the breaking point (Table III). Nylon has the lowest permanent set of the significantly extensible fibers tested (28% of the total elongation at break, Table II). Only Vinyon CF-HST (No. 15), wool (No. 21), and polyethylene A (No. 25) are comparable to nylon with respect to high extensibility and low permanent set, but these fibers have much lower tenacities. The immediate elastic recovery of nylon is not unusually high, the actual value being 4.2% at the breaking point, which corresponds to only 25% of its total recovery and 18% of its total elongation (Table V). Its delayed

* Fiber V is a Du Pont experimental fiber [3, 5]. It is now designated as "Dacron polyester fiber," and the fiber of the same chemical composition is known in Great Britain as Terylene [10].

recovery of 12.6%, however, is high, corresponding to 75% of its total recovery and 54% of its total elongation at the breaking point. Nylon does not have the disadvantages of poor extensibility, which characterizes other strong and elastic fibers, such as Fiberglas and Fortisan. From the molecular standpoint, nylon consists of a series of short hydrocarbon springs united by strong cross-linkages. These are responsible for the high recovery and low permanent set since they prohibit significant slippage of the long-chain molecules.

The recovery of nylon as compared to Orlon acrylic fiber (No. 12) [23, 32] and Fiber V (No. 13) may be of some interest since these are relatively new synthetic fibers of high quality. Graphs Nos. 12, 13, and 18 of Figure 7B represent the recovery behavior of the fibers and show the progressive increase in both extensibility and tenacity from Orlon acrylic fiber to Fiber V to nylon 300. The first two fibers exhibit similar recovery, markedly different from the behavior of nylon. This is demonstrated in Table V, where the actual as well as the relative values of recovery data for the 3 fibers at the breaking point are shown. It should be noted that Orlon acrylic fiber and Fiber V differ from nylon in that their actual values for immediate elastic recovery, delayed recovery, and total recovery (3a, Table V) are lower. The relative values of delayed recovery and total recovery expressed as percentages of the total elongation (3b) are nearly the same for these two fibers and are considerably lower than the corresponding values for nylon.

The extremely high delayed recovery of nylon contributes to seam puckering frequently observed when nylon threads are used [14, 36, 37]. Puckering is due in part to the tendency of nylon to creep back after being elongated in the stitching process. The difficulties encountered can be overcome to a certain extent by reducing the extensibility of nylon, but they cannot be entirely eliminated thereby. Fiber V has been shown to be superior to nylon in sewability [36]. This is due partly to the fact that the actual as well as the relative values of delayed recovery are markedly lower for Fiber V than for nylon. In addition, Fiber V, with a higher "modulus of elasticity"—as is clearly shown by the steep initial part of the stress-strain curve (Figure 6)—is less elongated than nylon by a given stress in the sewing operation. This comparison indicates that an excess of delayed recovery is undesirable for this particular application. The cause of sewing difficulties is still an open question because of the complexity and severity of this process. In sewing, both thread and fabric are subjected to high strain rates and high temperatures. However, consideration of recovery may help to solve some of the controversial problems involved.

F. Vinyon CF-HST

The recovery behavior of Vinyon CF-HST (No. 15) is remarkable for its similarity to nylon, having a low permanent set, high recovery, and especially high delayed recovery. Although the extensibility and breaking tenacity of Vinyon CF-HST are fairly high, they are not as high as those of nylon.

G. Vinyon NOZZ and NORU

Vinyon NOZZ and NORU are copolymers chemically different from Vinyon CF-HST; therefore, no correlation of their tensile properties was made.

The shrink-resistant Vinyon NORU (No. 20) was extended about 1300% and then heat-treated without tension at 135°C [4, 19]. This sample shows a somewhat lower tenacity and higher extensibility than Vinyon NOZZ (No. 9), which was extended to the same amount, but was not heat-stabilized and therefore not made shrink-resistant. Relative values of the elongation components are similar for both fibers at comparable levels of strain, but are quite different when compared at the same stress values. The permanent set of Vinyon NORU begins, however, at a lower strain and stress according to the lower yield point of this sample (Figures 6 and 7B).

H. Wool

The high "elasticity" of wool is one of the most important differences between this and other textile fibers and is responsible for the characteristic "softness" or "hand" of woolen fabrics. Wool (No. 21) has a higher extensibility than any other natural fiber tested. These valuable properties are produced partly by the peculiar morphology of wool fibers (scales and crimp) and partly by the inherent properties of the wool substance. Wool fibers consist of polypeptide chains held together by salt linkages, cystine linkages, and hydrogen bonds. The high recovery of wool is produced by strong cross-linkages and by the flexibility of the long-chain molecules.

In unextended fibers these molecules are coiled, and they are uncoiled as the fibers are stretched. The cross-links remain unbroken during this process and they prevent the chain molecules from slipping completely over each other. They assist greatly in the restoration of the initial structure after stress is removed. Only a minor portion of the high total recovery of wool (Table III) was found to be immediately recoverable at the breaking point. As in nylon 300, most of the total recovery consists of delayed recovery. This similarity can be understood from the resemblance of their molecular structure.

I. Casein

The extensibility and tenacity of the man-made protein fiber casein (Nos. 22 and 23) are very similar to wool. The recovery of casein fibers remains, however, markedly below the excellent recovery of wool, and a large portion of the high total elongation at the breaking point is permanent set (Table III).

Raw and stabilized casein multifilaments have not only almost the same breaking tenacity and total elongation at break, but also their recovery behavior is similar. Stabilization by formaldehyde has little effect on the tensile properties in the dry state.

J. Polyethylene

Polyethylene A (No. 25) and B (No. 24) were obtained from the same base material, polyethylene C, by a cold drawing process in which they were stretched nearly 600%. Type A was then relaxed 10% to 12% to increase its shrink-resistance [13]. This process is known as controlled shrinkage. Type B received no such treatment and thus was more highly oriented but less shrink-resistant.

The somewhat higher tenacity and lower extensibility of Type B are to be expected in view of the higher orientation of this sample. Although the stress and strain values are fairly close together at the breaking point, the relationship between stress and strain is very different for both types. This is illustrated by the two stress-strain curves in Figure 8. The distinct yield point of Type B at a relatively high stress value is remarkable. A considerable difference exists in the recovery of both types as a result of their history. Actual values of immediate elastic recovery at the breaking point for both samples are relatively high and similar. Immediate

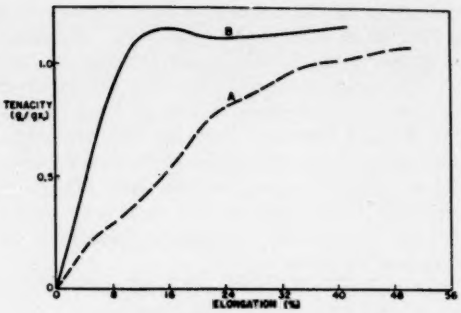


FIG. 8. *Stress-strain curves of polyethylene.*

elastic recovery increases at the very beginning of the stretching process until in the neighborhood of the yield point a maximum of nearly 80% of the actual total elongation is reached (Figure 7B). Then it decreases steadily to 10% at the breaking point. In contrast to this, the delayed recovery and permanent set of both samples are different. Type B does not show the previously described constancy of delayed recovery which was found for all the other fibers tested. At the breaking point the delayed recovery of Type B is markedly lower than that of Type A (Table II). The permanent set of Type B starts at a higher stress and strain by virtue of the high yield point. However, at higher strain values the permanent set of Type B markedly exceeds that of Type A when compared at the same level. Higher permanent set values for highly oriented polyethylene are contradictory to any experience with oriented fibers of viscose or acetate since the alignment of long particles makes further orientation impossible, strengthens the fiber, and thus prevents slippage, or permanent set, and reduces extension.

This unusual behavior of polyethylene is explained by the x-ray diffraction patterns of both samples shown in Figure 9. They reveal the following facts:

1. Both types are highly crystallized since they give distinct x-ray diffraction patterns.

2. The proportion between the crystalline and amorphous parts is nearly the same in both samples because the relative intensity of the diffraction spots and of the "amorphous ring" is not markedly different.

3. The orientation corresponds in both samples to the fiber axis or to the [001] direction of the crystal

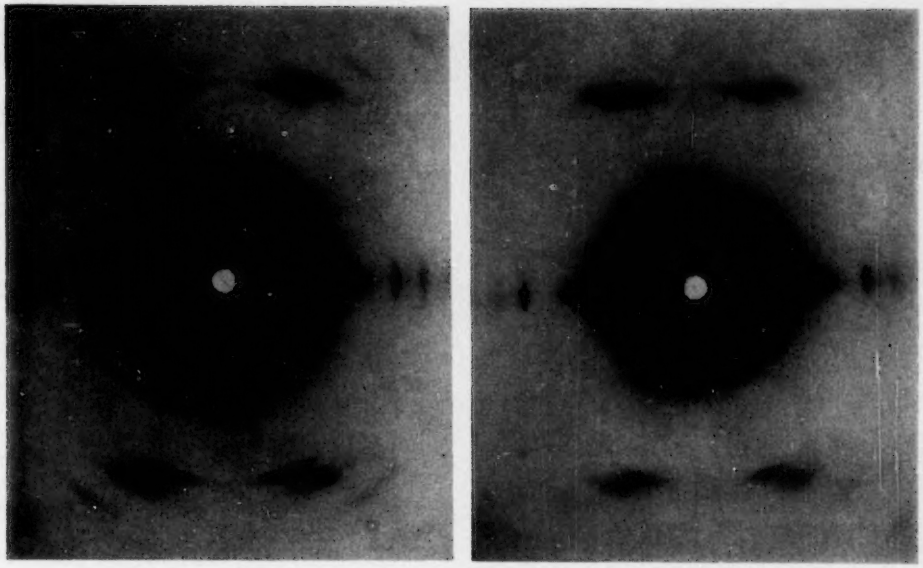


FIG. 9. *X-ray diffraction patterns of polyethylene. Type A—Left. Type B—Right.*

lattice. This is important since orientation along the [011] axis has also been observed in stretched polyethylene after relaxation [8] and this could affect markedly the tensile properties of such a fiber.

4. The degree of orientation is high and similar for both samples.

5. The crystalline part of Type B shows lattice defects, as indicated by the fuzziness of the diffraction spots, whereas no lattice distortion is observable on the clear x-ray diagram of Type A. The defects are a result of the cold drawing process. It is known that other cold-drawn materials, such as metals, show local displacement of atoms and formation of internal spaces, observable by the fuzziness of the x-ray pattern. Similar "destruction" of the crystal lattice during the stretching process was recently described [24] for nylon 300, when the yield point was exceeded (at an elongation of approximately 15%). It appears as a broadening of the diffraction lines on the x-ray diagrams of highly extended fibers, which can be interpreted as inhomogenous lattice defects or as decreased particles. Analogous observations have been made on metals at small plastic strains. The distortion of the crystal lattice is eliminated by the described controlled shrinkage of Type A, probably effectuated by moderate heating, by permutoid swelling, or by both. This procedure is analogous to the recrystallization of metals by annealing, where internal stresses are removed by heat treatment.

The x-ray diagrams of polyethylene A and B reveal that the main difference between the 2 samples is the presence of lattice defects in Type B. This explains the unusual recovery behavior and high permanent set of the highly oriented Type B, since structural defects and internal spaces intensify the slippage when stress is applied and this is always connected with a nonrecoverable elongation, or permanent set.

X. Comparison of Results with Those of Previous Investigators

Recovery data obtained in this study can be compared with data of other authors, such as Meredith, Maillard and coworkers, and Hamburger, only to a limited degree.

A. Meredith (1945)

Meredith [30] measured the recovery behavior of many single fibers from the beginning of stress up to

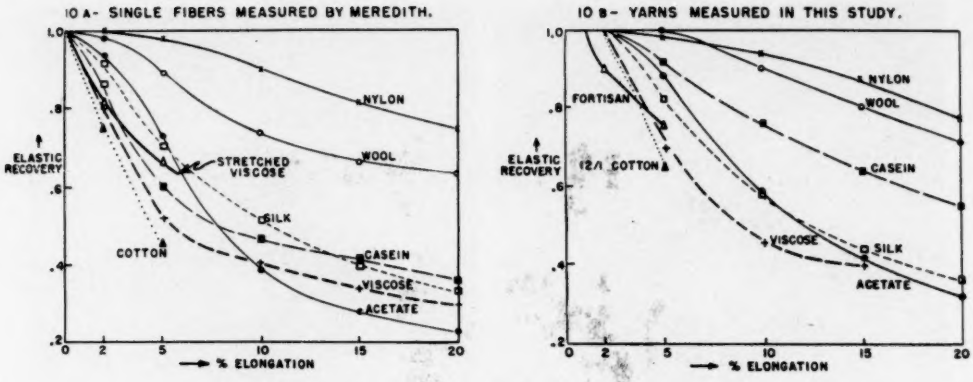


FIG. 10. *Recovery-strain curves of various filaments.*

rupture. He demonstrated the correlation between "elastic recovery" and stress or strain by means of "elasticity stress" and "elasticity strain" curves. "Elastic recovery" is the ratio of recoverable elongation to total elongation. It is closely related to the term "total recovery" (T.R.) used in the present study, which is the sum of immediate elastic recovery (I.E.R.) and delayed recovery (D.R.) when these are expressed as percentages of the actual total elongation:

$$\text{Elastic recovery} = \frac{\text{T.R.}}{100} = \frac{\text{I.E.R.} + \text{D.R.}}{100}.$$

The elastic recovery of acetate multifilament (No. 16), for example, as demonstrated in Table II and Figure 7B, is 1.00 at 50% of the tenacity at break, 0.58 at 50% of the total elongation at break, and 0.30 at the breaking point, since the values for immediate elastic recovery and delayed recovery are shown as 74% and 26%, 26% and 32%, and 14% and 16%, respectively, in columns 9, 10, and 11 of Table II. These data are higher (especially at 50% of tenacity) than Meredith's values for the acetate single fibers Seraceta (3.9 grex) and Celanese (1.1 grex). Besides some possible differences in the samples, variations in loading techniques might be responsible for this discrepancy.

Despite considerable differences in the two techniques used and in the samples tested, it is worthwhile to compare Meredith's results with the present recovery data since in both investigations many materials possessing widely different properties were tested.

In Figure 10A Meredith's data of "elastic recovery" for nylon, wool, casein, silk, viscose, acetate, stretched viscose, and cotton are plotted against strain. The data are taken from Table VIII of Meredith's paper [30] and represent average values obtained on single fibers at 2%, 5%, 10%, 15%, and 20% total elongation. In Figure 10B recovery-strain curves are demonstrated for the corresponding yarns as obtained directly from the upper rectangular graphs Nos. 18, 21, 22, 14, 10, 4, 16, and 5 of Figure 7B. Meredith's curves for viscose, stretched viscose, and cotton have been correlated to multifilaments of high-tenacity viscose (No. 10), high-tenacity Fortisan (No. 4), and 12/1 cotton staple yarn (No. 5), respectively, since their elongations at break are closest to the extensibility of Meredith's samples. The two sets of recovery curves in Figures 10A and 10B show that the agreement is surprisingly good between Meredith's data and those in the present paper, despite marked differences in the tests. Meredith's "elastic recovery" values are generally lower than ours, particularly at 2% elongation. This deviation can be explained by the differences in the loading technique.* The discrepancy between the two casein curves is most likely caused by differences in the properties of the samples tested.

* In Meredith's test a lower jaw speed was used. The samples were held extended 30 sec., and only 60 sec. relaxation time was allowed for recovery. All these factors increase the "permanent set" and decrease the "elastic recovery" as compared to the conditions of our tests (immediate removal of elongation and 300 sec. relaxation time). Consequently, an "elastic recovery" of 1.00 was observed for most fibers at 2% elongation in our tests.

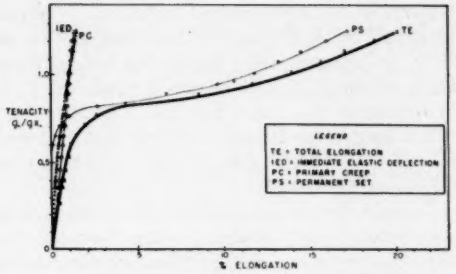


FIG. 11. *Stress-strain curves of acetate multifilament 300/104/1.5. (Measured by W. J. Hamburger.)*

The exceptional high recovery of nylon, the similarity of nylon and wool, and the inferiority of casein to wool with respect to recovery are also shown by Meredith's curves. However, no information is provided by these tests on the "quality" of the recovery since no differentiation was made between immediate and delayed recovery.

B. Maillard and coworkers (1947–48)

Seven of the fibers tested in this study were also investigated by Maillard and coworkers [26, 27]: cotton, regular and high-tenacity viscose, silk, acetate, nylon, and wool. The agreement between the results for total recovery at the breaking point is fairly good. The insignificant deviations are probably due to differences in the testing methods or in the inherent properties of the samples tested.

C. Hamburger (1948)

Some data of immediate elastic recovery and delayed recovery obtained in this study can be compared to those of "immediate elastic deflection" and "primary creep" of Hamburger [20, 21]. Despite the marked difference between the pulse-propagation technique and the repeated-loading technique, and also between the methods of evaluation, Hamburger's data for viscose, acetate, and nylon are similar to ours.

It is worth-while to demonstrate data obtained on acetate multifilaments by the pulse-propagation technique and by the repeated-cycling method used in the present study for purposes of comparison, even though the samples tested were different.

The values demonstrating the visco-elastic behavior of 300/104/1.5 Tennessee Eastman acetate

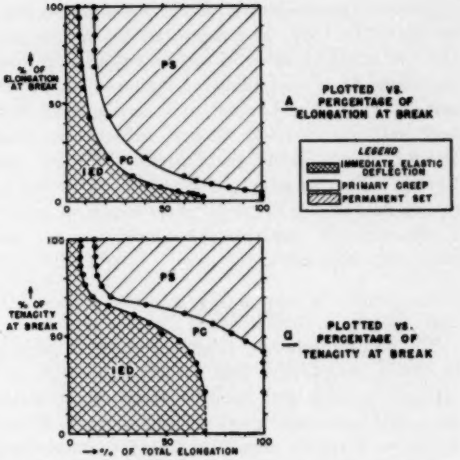


FIG. 12. *Quadratic graphs showing elongation components of acetate multifilament 300/104/1.5. (Measured by W. J. Hamburger.)*

multifilament as obtained by the pulse-propagation meter * are replotted in Figure 11, by means of four curves, and in Figures 12A and 12a, by means of two quadratic graphs.

These figures should be compared with Figures 4D, 5D, and 5d, which demonstrate the recovery data obtained in the present investigation on 100/40/2.5 Acele, Du Pont acetate multifilament (No. 16), using sustained elongation instead of the normal, immediate removal of elongation. This variation of our test conditions corresponds nearly to the conditions of Hamburger's tests, in which the immediate elastic deflection and the primary creep were measured on the sixth loading cycle. It is known that repeated stressing and sustained elongation produce a similar effect on the tensile properties. Comparison of the two sets of curves and graphs shows that Hamburger's data of deflection components correspond fairly well to our elongation components. This good agreement between actual as well as relative values of the three components obtained by tests made on different samples using different testing methods proves that data of the three components are indeed representative of inherent fiber properties.

* These were presented by Hamburger in Graph 11c, p. 732, of his paper in TEXTILE RESEARCH JOURNAL [20] and were also shown in Figure 5, p. 496, of his condensed article in the *A.S.T.M. Standards* on Textile Materials [21].

Similar agreement was found for total recovery by Meredith [30], who compared his results with those of a large number of early investigations made on single fibers and yarns of cotton, silk, viscose, acetate, wool, and Lanital published between 1927 and 1943 by Shorter, Collins, Küsebauch, Saxl, Langer, Kurts, Böhringer, Schwab, Weltzien, and Loasby. This agreement also indicates that the recovery behavior of fibers is by no means as subject to variation in particular test conditions as was frequently believed.

XI. Summary

The cycling technique described makes it possible to obtain comparable data on the immediate and delayed recovery and the permanent set of textile fibers and yarns, and gives a more accurate characterization of tensile properties than the conventional stress-strain curve. The method as applied to measure the recovery behavior may have some inadequacies which will be eliminated by improved equipment. The recovery data obtained can serve as a basis for further investigations on fibers, yarns, and fabrics since they indicate the applicability of these textile materials for specific end-uses. The knowledge of recovery also provides a better understanding of the complex behavior of textile materials and their practical implications.

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Improvement of Cotton Cloth in Resistance to Soiling and in Ease of Washing*

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Abstract

The general problem of producing resistance to soiling in cotton textiles is presented, and the effects of a number of treatments upon the ease of soil acquisition by cotton cloth and upon the ease of soil removal from the soiled cloth by washing are described. Of the treatments employed, those which altered the electrical charge upon the cloth by introducing acidic groups appeared to have the most favorable general effect in increasing soiling-resistance and ease of soil removal. A partial-acetylation treatment was noticeably effective in increasing resistance to dry soiling.

Introduction

In recent years, interest has increased in an important practical textile problem—the treatment of cotton cloth so as to confer upon it superior resistance to soiling and/or superior ability to be cleaned by a washing process. In 1948 the United States Department of Agriculture began sponsorship of a research contract with the Institute of Textile Technology for work upon this general problem. The present paper describes the experimental work carried out during the period June 1948–August 1949. An account of some of the general aspects of the problem of soil-resistant cotton—fields of application, hypothetical means of solution, limitations of treatment, reasons for choice of experimental materials and methods, and comparisons of laboratory and end-use means of producing textile soiling—has recently appeared [5], and will therefore not be repeated here.

Very little literature on the problem of producing resistance to soiling or ease of cleaning of cotton cloth has appeared. Two early patents [1, 2] pointed out the easy washability of cotton fabrics coated with nitrocellulose lacquers. Stout and Schiermeier [4] and Krüger [3] discussed the effect of previous starching on the ease of soiling and of washing cotton fabrics. These investigators found that cloth containing 5% or more starch was more darkly soiled than unstarched cloth from carbon tetrachloride dispersions of lampblack. They attributed this effect to a filtering action which brought about a concentration of soil on the surface of the starched cloth. The soil was more readily removed, however, from starched than from unstarched cloth. Presumably, the starch was largely removed during the washing.

Numerous trade articles and advertisements concerned with various cotton textile water-repellent treatments have claimed fabrics so treated to be resistant to aqueous soil dispersions, and, in some cases, to be easily cleaned when soiled by such materials. No work appears to have been published, however, on the behavior of such treated fabrics toward the acquisition or removal of other (non-aqueous) types of soil.

Among the treatments which were applied to cot-

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ton cloth in the present study were the following: various amounts of moisture; various amounts of starch; cationic and anionic softening agents; durable and nondurable hydrophobic finishes; emulsions of pre-polymerized vinyl polymers; urea and melamine-formaldehyde condensates polymerized in the cloth; and treatments such as partial acetylation or partial carboxymethylation producing chemical alterations in the cotton cellulose. The effect of these upon the action of liquid-dispersed soils for both carbon tetrachloride and aqueous pigment dispersions and upon the ease of acquisition of dry soils is discussed in the Results section.

Experimental Methods and Materials

In general, the experimental methods and materials employed were like those used in previous work in this laboratory [6, 7, 8]. In order to cover a reasonable amount of ground in a limited length of time, a number of the possible experimental variables, such as types and quantities of detergents, were selected arbitrarily. These selections were made in an effort to attain maximum coverage of the conditions most convenient for laboratory experimentation or (more important) most representative of end-use conditions.

The cloth was a bleached, kiered, desized 80 × 80 cotton nainsook sheeting.

Pigment (Germantown Lampblack No. 12, Aquablak B (after evaporation of the water present in the commercial product), or Mapico Black magnetic iron oxide) was stirred or ground with a mixture of Nujol mineral oil and Snowdrift shortening to make a soiling paste. A weighed quantity of such a paste was dispersed in carbon tetrachloride or in a mixture of *n*-butanol and dioxane to give one type of soiling mixture. These pigments and soiling mixtures have been described previously [7, 8]. Aqueous soil dispersions were prepared by simple dilution of the commercial Aquablak B paste with water, or by ball-milling the Germantown lampblack (100 parts) overnight with Daxad 23, a commercial dispersing agent (about 10 parts), in water (about 3,000 parts). Stable aqueous dispersions of the iron oxide pigment could not be prepared in this manner. Dry soiling was done with the lampblack and with the screened, sifted material collected by a vacuum sweeper from the carpets of a local theater. This latter soil was brown in color rather than grey or black.

The general methods of application of soiling mixtures (liquid dispersions), washing of soiled cloth, and estimation of appearance or of soil content were essentially the same as described earlier [8]. The extent of visible soiling produced by passing strips of the untreated cotton cloth through an arbitrary concentration (usually about 1%) of soiling paste or pigment in a dispersing liquid was taken as a standard, and a similar visible extent of soiling was produced on the treated cloth in question by suitable

TABLE I. DETERGENTS SELECTED FOR SOIL-RESISTANCE WASHING TESTS

Type	Trade name
1. High-grade unbuilt soap for home use	Ivory Snow
2. High-grade built soap for home use	Oxydol
3. Built synthetic detergent for home use (except rotary-type washers)	Tide (alkyl sulfate)
4. Built synthetic detergent for rotary-type home washers	All (nonionic)
5. Unbuilt soap detergent for commercial laundries	Arctic Crystal Flakes
6. Built soap detergent for commercial laundries	Ozonite

TABLE II. COMMERCIAL PRODUCTS USED FOR CLOTH TREATMENT

Trade name	Type
Ahcovel A Atcosoft SD Quaker TT 4041 Onyxsan LG Onyxsan S	Cationic softener
Ahcovel F Atcosoft AS Mapromol HSY Quaker TT 4052	Anionic softener
Dow-Corning 1107 Norane	Durable hydrophobic finish
Atco Dri Drax	Nondurable hydrophobic finish
Kandar Polyvinyl acetate (Elvacet) Five Polyco resins Four Rhoplex resins Xyno Resin AA 40	Pre-polymerized vinyl resins (neutral)
Atco D-88	Pre-polymerized vinyl resin (poly acid)
Two Rhonite resins	Formaldehyde-condensate resins

adjustment, if necessary, of the concentration of pigment soil in the dispersing liquid; the treated and untreated strips were passed through the soiling apparatus at the same rate of speed for an equal number of times.

Dry soiling was done by tumbling treated and untreated 3-in. swatches of cloth with rubber stoppers and a suitable amount of dry soil in a jar designed for dynamic water-absorption tests upon textiles. The soiled swatches were shaken in a sieve and then brushed gently to remove excess soil.

The detergents, cloth treating agents, etc., were obtained directly from the manufacturers, and were used as received. Table I lists the types and trade names of the various detergent products used in most of the work. The cloth treating agents are listed in Table II. The use of any particular product or treating agent is not to be interpreted necessarily as a recommendation of that product or agent by the authors, in preference to other materials of similar type that are also commercially available.

Experimental Results and Discussion

Liquid-Dispersed Soils

In the following presentation of experimental work, the effect on both the ease of soiling and the ease of soil removal produced by a given type of cloth treatment will be discussed before continuing to another treatment. In the interest of brevity, the experimental data presented for a given treatment represent averaged or representative values.

Humidity and Moisture.—Strips of the test cloth were brought to equilibrium conditions in atmospheres of 35%, 60%, or 85% relative humidity, either by static exposure for several days or by more rapid conditioning in a forced-ventilation box (atmospheric temperatures 70°–75°F). All conditioned strips were stored until the time of their soiling in a can with a tight top in the atmosphere to which they had been exposed. A conditioned strip from each humidity exposure was given an equal exposure to each of the three following soiling mixtures:

(*a*) A dispersion of lampblack, mineral oil, and vegetable oil in carbon tetrachloride (in which water is only slightly soluble);

(*b*) A dispersion of the same ingredients as above in a 50:50 mixture by volume of *n*-butanol and 1,4-dioxane (in which water is soluble);

(*c*) A dispersion of Aquablak B in water, applied by the padding method or by a tumbling procedure in pint jars in the Launder-Ometer.

Each strip in this and in succeeding series of experiments was passed through both the dispersion and the padder rolls three times (total exposure time was of the order of 10 to 20 sec.), dried in the laboratory air, baked in an oven 30 min. at 71°C, and stored over anhydrous calcium chloride in a tight can. The three strips with different conditioning environments soiled to about the same visible extent when passed through a given soiling dispersion, although their moisture contents at the time of soiling varied from about 5% to about 12%.

These soiled strips (and also those in the later experiments described below) were cut into 3-in. square swatches, the swatches were sorted according to their individual percentage reflectance values, and pieces of equal reflectance were selected for comparative behavior during washing. The general washing procedure consisted of two 10-min. washings in a 0.25% dispersion of detergent in the Launder-Ometer. The machine speed was 42 r.p.m. and the temperature 140°F. Forty ¼-in. steel balls, 200 ml. of detergent dispersion, and four swatches of cloth were placed in each jar. Ivory Snow, Duponol ME, and Nacconol NR were used as the detergents in these particular tests. Local municipal water, containing 16–18 p.p.m. hardness, was used for all washings.

In each set of swatches which had been soiled by the same pigment dispersion and washed with the same detergent, the extent of soil removal by washing was the same (as estimated by reflectance measurements) within experimental error, despite the differences in the relative humidity to which they had been exposed.

This sameness of soiling and washing behavior in the pieces conditioned under different humidities led to a selection of more extreme moisture environments to which to expose cloth prior to soiling. One new group of clean strips was stored in an oven at 105°C until constant weight was attained, while a second new group of strips was wet thoroughly and then spun as free of water as possible in the centrifugal unit of a home-type washing machine. The moisture contents of these two sets of strips were about 0% and 75%, respectively. These strips were then soiled by the padding method with the same dispersions as used before. With all three

TABLE III. REFLECTANCE VALUES AND RELATIVE IRON OXIDE SOIL CONTENTS BEFORE AND AFTER WASHING OF SWATCHES OF COTTON CLOTH SOILED WHEN DRY OR WHEN DAMP IN CCl_4 DISPERSIONS OF MAPICO BLACK

Cloth treatment	Detergent	Average reflectance		Relative iron oxide content	
		Before washing (%)	After washing (%)	Before washing (mg./2 g. cloth)	After washing (mg./2 g. cloth)
Soiled dry	Ivory Snow	30	63.5	10.4	1.6
Soiled damp	Ivory Snow	30	76.3	13.2	0.27
Soiled dry	Tide	31	66.4	9.3	1.4
Soiled damp	Tide	31	72.7	16.1	0.53

soiling dispersions, similar results were obtained: the dry pieces soiled much more heavily than did the damp pieces. In one typical experiment, dry cloth with an initial reflectance of 82% had a reflectance of 24% after soiling, while damp cloth of the same initial reflectance had a reflectance of 40% after soiling under equal conditions.

In order to compare the ease of soil removal from cloth soiled while dry or damp, the soiling procedure was repeated, adjusting the concentrations of the soiling dispersions so that the reflectance values of the dry and damp cloth strips soiled in a given dispersion were equal. This required the use of a higher (3 to 6 times as much) soil concentration in the dispersions used on damp cloth than in those used on dry cloth. Pieces soiled by each of the three different dispersions were washed as before, using the same three detergents. For each of the nine pairs of test pieces, the extent of soil removal from the pieces which had been soiled while damp was greater than it was from the pieces soiled while dry or soiled after acquiring 5% to 12% moisture by exposure to the various environments.

In one typical experiment, pieces of soiled-dry cloth changed from 33% to 62% reflectance upon being washed; the change for soiled-damp cloth given an equivalent washing was from 33% to 74%.

A set of test pieces was also exposed to an aqueous Aquablak B dispersion by tumbling in a Launder-Ometer jar for 15 min.; in this case a different result was obtained—all of the pieces emerged with practically the same extent of visible soiling, despite the range from 0% to 75% in their initial moisture contents. Moreover, the soil removal by washing from these soiled pieces was about equal with each of the three detergents named above.

A dispersion of Mapico Black (magnetic black iron oxide) pigment and oils in carbon tetrachloride was then used to soil dry and damp strips of cloth. The damp strips were comparatively quite resistant to soiling, and it was found necessary to use a pigment dispersion of about 15 times normal concentration in order to soil the damp strips to the same visible extent as had been needed for the dry strips. Table III shows the reflectance values and relative iron oxide contents of the dry-soiled and damp-soiled pieces before and after washing.

The unwashed swatches of cloth soiled when damp presented a somewhat speckled appearance, apparently due to flocculation of the soil. As would be expected from this observation, analyses showed that the damp-soiled cloth contained more pigment than did the dry-soiled cloth of equal average reflectance. After washing, however, both reflectance measurements and iron oxide analyses showed the once-damp cloth to be cleaner, although it had contained more soil prior to washing.

The damp cloth appeared to resist soiling from liquid dispersions because the water already present prevented displacement by the soil-dispersing liquid, even when the latter was water, except for a long time of exposure. Of course, in practical end-use exposure to dry soil, damp cloth acquires soil more readily than does dry cloth. It is thought that the damp-soiled cloth washed cleaner than the dry-soiled cloth because the pigment soil had neither become absorbed nor penetrated the fabric surface as readily as had occurred with dry cloth.

As the earlier portion of the above-described experiments indicated that soiling at various times with atmospheric relative humidities varying from 35% to 85% produced cloth of the same extent of soiling and of the same ease of soil removal by washing, subsequent soiling work reported in this paper was done in an ordinary laboratory atmosphere of non-regulated humidity.

TABLE IV. REFLECTANCE VALUES BEFORE AND AFTER WASHING OF SWATCHES OF COTTON CLOTH TREATED WITH DISTILLED WATER OR HARD WATER, AND SOILED WITH CCl_4 DISPERSIONS OF LAMPBLACK

Cloth treatment*	Detergent	Reflectance before washing (%)	Average reflectance after washing (%)
S	vory Snow	24	57.4
D		24	57.7
H		24	56.8
S	Tide	24	60.4
D		24	62.5
H		24	59.6
S	Fab	24	54.4
D		24	58.3
H		24	58.3
S	All	23	53.9
D		23	57.9
H		23	57.6
S	Oxydol	23	56.4
D		23	57.5
H		23	56.3
S	Ozonite	23	53.2
D		23	55.3
H		23	55.9

**S*—Standard untreated. *D*—Distilled water. *H*—Hard water.

TABLE V. REFLECTANCE VALUES BEFORE AND AFTER WASHING OF SWATCHES OF COTTON CLOTH TREATED WITH DISTILLED WATER OR HARD WATER, AND SOILED WITH AQUEOUS DISPERSIONS OF LAMPBLACK

Cloth treatment*	Detergent	Reflectance before washing (%)	Average reflectance after washing (%)
S	Ivory Snow	26	43.4
D		26	48.0
H		26	43.0
S	Tide	27	45.8
D		27	48.5
H		27	43.0
S	Fab	27	44.3
D		27	48.5
H		27	44.8
S	All	29	45.8
D		29	47.3
H		29	44.1
S	Oxydol	28	45.0
D		28	47.1
H		28	41.8
S	Ozonite	28	42.3
D		28	46.8
H		28	41.3

* *S*—Standard untreated. *D*—Distilled water. *H*—Hard water.

Calcium and Magnesium Salts.—One group of strips of clean standard cloth was soaked in distilled water, and another in synthetic hard water containing sufficient calcium and magnesium salts to produce 300 p.p.m. hardness. The wet strips were wrung out and allowed to dry in the laboratory air. Dried strips from these two treatments were exposed in the usual way to dispersions of lampblack in carbon tetrachloride or in water. Their extent of soiling was the same.

Swatches of matching reflectance were chosen and washed in dispersions of the various detergents listed in Table I, along with swatches of soiled cloth which had not been given any soaking treatment prior to soiling. The reflectance values before and after washing are shown in Table IV for swatches soiled from carbon tetrachloride and in Table V for swatches soiled from water.

The presence of the calcium and magnesium salts did not appreciably alter the ease of removal of the soil applied from either carbon tetrachloride or water, compared to soil removal from untreated standard cloth. The amount of exposure to calcium and magnesium ions which the cloth had received during manufacture and finishing prior to being used in this work was not known.

Soaking in distilled water prior to soiling produced an improvement in the ease of removal of the soil applied from water.

Starch.—It was decided in this work to study the effect of lower, more practical concentrations of starch than those used by earlier investigators [3, 4]. Most of the work was done with a 40-fluidity Clinton modified starch, of a type often used for cotton warp sizing, in concentrations from 0.5% to 5%. The starches were prepared in aqueous dispersions by 15–20 min. of stirring at near-boiling temperatures, and were used immediately to treat standard strips of cloth, by dipping followed by centrifugal extraction of excess liquid. Starch contents of the treated cloths were estimated by weight measurements of air-dried strips before and after exposure.

Strips of the various starch-treated cloths and of the untreated cloth were soiled by the usual padding procedure with dispersions of the lampblack-oils paste in carbon tetrachloride or of lampblack in

TABLE VI. QUALITATIVE EFFECT OF STARCH ON EASE OF SOILING AND WASHING OF COTTON CLOTH

Amount of starch (%)	Soil applied from	Effect on soiling*	Effect on washing*
Up to 1.5	CCl_4	Slightly darker	Little effect
	Water	No effect	Soaps—little effect; other agents—darker
5	CCl_4	Darker	Lighter
	Water	Slightly darker	Soaps—lighter; other agents—little effect

* Compared to results with untreated cloth.

water. The starched pieces soiled somewhat more heavily than unstarched pieces from the carbon tetrachloride dispersions; this was more noticeable with the highest (5%) starch concentration. Starch had a slight or zero effect upon the extent of visible soiling from the aqueous pigment dispersions.

Pieces of the strips of soiled cloth containing from 0% to 5% starch were washed in dispersions of the standard detergents. Qualitative effects of starching on the ease of both soiling and washing of the test cloth are summarized in Table VI. It appeared that the effect of starch on the ease of washing depended upon the amount of starch on the cloth; relatively small amounts of starch hindered the removal of visible soil or at least did not aid it, while 5% of starch was of definite aid to washing (except for the nonsoap detergents on aqueous-soiled pieces). In the work of Stout and Schiermeier, all of the starch concentrations on cloth were above 5%, and all the starch-treated pieces came out brighter than the untreated ones. The fact that small amounts of starch appeared to slightly hinder the removal of pigment soil, while large amounts appeared to aid its removal, suggests that more than one mechanism of soil attraction and adhesion may have been operating.

In order to study these effects further, strips of cloth containing 1.5% starch were exposed to a dispersion of the Mapico Black iron oxide pigment in carbon tetrachloride. The starched pieces soiled a little (about 1.5 reflectance percentage units) darker than the unstarched pieces. Washings were done on soiled pieces of starched and unstarched cloth of matching initial reflectance. Analyses for iron content were made on representative pieces before and after washing. The reflectance values and relative iron oxide soil contents for these pieces of cloth after washing in Ivory Snow and Tide are given in Table VII.

TABLE VII. EFFECT OF 1.5% STARCH ON EASE OF REMOVAL OF MAPICO BLACK PIGMENT PUT ON COTTON CLOTH FROM A CCl_4 DISPERSION (WASHED IN 0.25% DETERGENT DISPERSION)

Cloth treatment	Average reflectance		Relative iron oxide content	
	Before washing (%)	After washing (%)	Before washing (mg./2 g. cloth)	After washing (mg./2 g. cloth)
Ivory Snow				
Unstarched	32	65	7.9	0.99
Starched	32	68	9.5	0.62
Tide				
Unstarched	32	55	7.9	2.7
Starched	32	56	9.5	2.0

The iron oxide analyses of the unwashed soiled pieces indicated that the starched cloth contained more pigment than the unstarched cloth of equal reflectance. After washing, the once-starched pieces were somewhat better cleaned than the untreated pieces judging by the pigment content, although this difference was not definitely indicated by the reflectance values.

Cationic and Anionic Softeners.—The effects on soiling and washing produced by a number of the various cationic and anionic softeners on the market in 1949 were thought to be worth-while determining, since these treating agents were easy to apply, did not stiffen the cloth, and were substantive in that they were claimed to remain on the cloth to the extent of about 1% after laundering. The specific materials used are listed in Table II. These two types of softening materials might have been expected to confer electrical charges of opposite sign upon treated cloths, and thus alter the tenacity with which soil particles would be held, especially if these particles were also charged.

Strips of the test cloth were treated with moderate amounts of the softening agents by methods recommended by the manufacturers and exposed to the lampblack soiling dispersions in carbon tetrachloride or in water. As before, the concentration of lampblack in the soiling bath was adjusted, when necessary, to produce strips the apparent soiling of which was equal to that of the soiled but untreated standard

strips. Soiled swatches of equal initial reflectance were washed as usual in the standard detergents.

The cationic agents employed had similar chemical compositions and physical properties, and in general demonstrated similar behavior toward soil dispersions; three of the anionic agents also demonstrated similar general behavior, with Mapromol HSY varying in some respects from the others. The results of a number of soiling and washing experiments have been condensed into the qualitative values shown in Table VIII.

TABLE VIII. QUALITATIVE EFFECT OF SOFTENERS ON EASE OF SOILING AND WASHING OF COTTON CLOTH

Type of softener	Soil applied from	Effect on soiling*	Effect on washing*
Cationic	CCl_4	Lighter	Little effect
	Water	Darker	Much lighter
Anionic	CCl_4	Slightly lighter	Little effect
	Water	Lighter	Lighter

* Compared to results with untreated cloth.

Both the cationic and anionic agents caused treated cotton cloth to soil somewhat less dark than did the standard untreated cloth from carbon tetrachloride soil dispersions; the anionic agents had a similar effect with aqueous soil dispersions, but the cationic agents caused treated cloth to soil darker than did the untreated cloth from such dispersions. The two types of softening agents had a second similar effect on cloths soiled from carbon tetrachloride dispersions, in that they produced little or no change in the ease of visible soil removal by washing. Both types were definitely effective in improving the apparent ease of removal of aqueous-deposited soil. The cloth treated with cationic agents behaved toward aqueous soil as did starched cloth toward carbon tetrachloride-dispersed soil—in both cases, the treatment produced a greater ease both of soil acquisition and of soil removal. The single most striking effect produced by the use of this group of treating agents was the enhanced ease of removal of aqueous soil from cloth treated with the cationic softeners. This is especially interesting, as this type of soil has generally been found to be rather difficult to remove from untreated cotton cloth.

It should be emphasized again that interpretations of the results of experiments of this type must be made with care. If a piece of cloth, after treatment by a process that added a substance to the cloth, is exposed to a soiling dispersion, and emerges darker than does the standard untreated cloth exposed to the same soil, it has not necessarily acquired more soil. It may have done so; but, alternatively, it may have acquired only the same or even a lesser amount of soil, and may be holding the soil principally on the surface, where most of it is visible to a reflectance-measuring instrument. Thus, the apparent acquisition of soil, as indicated by reflectance measurements, may or may not correspond to the true increase in soil content. The same considerations also apply to the brightening of a piece of soiled cloth as a result of washing. However, as stated before [5], from the point of view of the consumer, appearance, and not true soil content, is the important property; thus the use of reflectance measurements as a principal criterion of the apparent usefulness of a given treatment in lessening soiling or in aiding soil removal appeared justified in this study.

Hydrophobic Finishes.—Four hydrophobic finishes, selected to be representative of the principal types available to textile finishers in 1949, were studied for their effect on soiling and on soil removal. Two were of the so-called "durable" type, which is heat-cured on the fabric and the effect of which endures through at least several launderings. Norane is of the quaternary pyridinium type, and Dow-Corning 1107 is a polymerizable silicone derivative. Two were of the "nondurable" type, which is applied without curing, and which largely washes out of the fabric during the first laundering to which it is exposed. Both of the latter materials used were wax emulsions designed for textile application.

Pieces of the standard cloth were given appropriate treatments with each of these four hydrophobizing agents as directed by their manufacturers and were exposed to the usual dispersions of lampblack in carbon tetrachloride and in water. As would be expected, the aqueous soil dispersions produced almost no lowering of reflectance in these water-repellent strips; hence, no washing tests were run on the cloths exposed to aqueous soils. These treatments also produced a substantial resistance to soiling from the carbon tetrachloride dispersions; two to four times the usual concentration of pigment in the soiling dispersion was needed with treated strips to produce reflectances matching the usual reflectance on untreated soiled cloth.

Washing pieces of the treated cloths soiled from

TABLE IX. REFLECTANCE VALUES AFTER WASHING OF SWATCHES OF COTTON CLOTH TREATED WITH VARIOUS HYDROPHOBIC FINISHES AND SOILED WITH CCl_4 DISPERSIONS OF LAMPBLACK

Cloth treatment	Reflectance (%) after washing* Ivory Snow	Tide
Untreated	57	59
Norane	46	35
Dow-Corning 1107	34	28
Atco Dri	53	50
Drax	63	59

* Reflectance before washing, 23%–25%.

carbon tetrachloride dispersions of lampblack produced rather interesting results (Table IX). The pigment soil on the cloths treated with the two durable water-repellents, which are not removed by one laundering, was quite poorly removed by washing. On the other hand, the pigment on the cloths treated with the nondurable wax-type repellents, which wash out during laundering, was removed about as well as from the untreated cloth. This unexpected retention of soil by the swatches given a durable hydrophobic finish was studied further by use of the black iron oxide pigment dispersed in carbon tetrachloride. Table X gives data for removal of this pigment from untreated swatches and from swatches treated with Norane, making use both of optical measurements and of analyses for iron.

Although the analyses on the unwashed treated and untreated pieces soiled to the same reflectance showed that the Norane-treated pieces contained less pigment, both reflectance measurements and iron oxide analyses on washed pieces showed the untreated cloth to have become cleaner than the Norane-treated cloth. Treated swatches soiled with the iron oxide and washed in Tide actually emerged with a lower reflectance after washing than before. A possible explanation for this behavior, and for the poor removal of lampblack from cloths treated with Norane or Dow-Corning 1107, is that the soil was originally deposited on the hydrophobic cloth in an agglomerated form, and that the washing bath first dispersed this dirt and then redeposited much of it in a more subdivided form which possessed an increased blackening power. It also appears possible that a durable water-repellent finish may cause the treated cloth to attract pigment particles in an aqueous detergent bath, perhaps by an alteration of

TABLE X. REFLECTANCE VALUES AND RELATIVE IRON OXIDE CONTENTS BEFORE AND AFTER WASHING OF SWATCHES OF COTTON CLOTH TREATED WITH NORANE, AND SOILED WITH CCl_4 DISPERSIONS OF MAPICO BLACK

Cloth treatment	Detergent	Average reflectance Before washing (%)	Average reflectance After washing (%)	Relative iron oxide content Before washing (mg./2 g. cloth)	Relative iron oxide content After washing (mg./2 g. cloth)
Untreated	Ivory Snow	33	65	7.7	0.94
Norane		33	44	6.9	2.8
Untreated	Tide	34	59	7.4	1.8
Norane		(1) 34	31	6.4	5.8
		(2) 32	28	—	—

surface electrical charges or by some type of preferential wetting action.

If these findings are correct, it would appear likely that hydrophobized fabrics in practical end-use, such as in tablecloths, raincoats, sport jackets, etc., would resist liquid-dispersed soiling more than would untreated garments, but after being soiled once by an oil-dispersed pigment would be hard to clean by washing. Advertising labels on such articles frequently point out their "spot-proof" qualities, but these claims are directed toward resistance to aqueous solutions and dispersions. Manufacturers' recommendations for cleaning of soiled raincoats and jackets made from hydrophobized cotton fabrics are generally for dry cleaning rather than for aqueous washing.

Resin Finishes.—A number of new textile-finishing resins in the form of emulsion polymers of fairly high solids content have appeared on the market in recent years. These are typically neutral polymers or copolymers of vinyl acetate, vinyl chloride, vinylidene chloride, styrene, the acrylates, etc. About a dozen of these resins of varying composition were applied to strips of cloth by padding from aqueous emulsions according to manufacturers' directions, and the usual soiling and washing procedures were carried out. The effect of the presence of a water-soluble vinyl resin of the sodium polyacrylate type was studied at the same time. Dry-weight pickup values of these resins varied from about 3% to about 6%, depending chiefly upon the concentration of resin used in the padding emulsion.

Because of the similarity of effects produced by the neutral resins, the results of soiling and washing

TABLE XI. QUALITATIVE EFFECT OF RESIN FINISHES ON EASE OF SOILING AND WASHING OF COTTON CLOTH

Type of resin	Soil applied from	Effect on soiling*	Effect on washing*
Emulsions of neutral addition polymers	CCl_4	Lighter	Much darker
	Water	Little effect	Much darker
Water-soluble (Na poly-acid type)	CCl_4	Lighter	Slightly lighter
	Water	Little effect	Much lighter

* Compared to results with untreated cloth.

TABLE XII. QUALITATIVE EFFECT OF VARIOUS ALTERATIONS OF CELLULOSE ON THE EASE OF SOILING AND WASHING OF COTTON CLOTH

Treatment	Soil applied from	Effect on soiling*	Effect on washing*
Mercerization	CCl_4	No effect	No effect
	Water	Lighter	Slightly lighter
Partial acetylation	CCl_4	No effect	Slightly lighter
	Water	No effect	Lighter
Partial carboxymethylation	CCl_4	Slightly lighter	Lighter†
	Water	Lighter	Lighter†
Partial aminoethylation	CCl_4	No effect	No effect
	Water	Slightly darker	Darker

* Compared to results with untreated cloth.
† Much darker with an alkylarylsulfonate detergent.

tests on cloths treated with them have been grouped qualitatively and are shown in Table XI, together with the results from the use of the water-soluble resin. The various neutral resins behaved like the durable hydrophobic finishes in that they produced resistance to soiling from carbon tetrachloride dispersions, and also caused the soil to be held rather tenaciously upon washing. The effect of these resins in producing resistance to acquisition of aqueous soil was erratic, but they had a uniform effect in causing the aqueous-deposited soil to be held tenaciously to the fabric during washing. The resin containing sodium carboxylate groupings, however, had a generally favorable effect upon soil deposition and removal, particularly in respect to the washing removal of soil deposited from aqueous dispersion.

The effect of two representative crease-resistant finishes of the urea-formaldehyde type was also determined. These did not produce any significant change in resistance to soiling, and made the acquired soil slightly more difficult than usual to remove. Tests with other finishing agents of this type should be studied.

Modification of Cotton Cellulose.—The final group of textile finishes studied consisted of treatments which altered the cotton cellulose chemically; these included mercerization, partial acetylation, partial carboxymethylation, and partial aminoethylation. These treatments were applied to the standard cotton cloth by the Southern Regional Research Laboratory. The use of such finishes was theoretically attractive in that they produce little or no undesirable change in appearance, hand, or other physical properties of the cotton fabric.

Mercerization was carried out under conditions which held the warp yarns, but not the filling yarns, under tension. The partial-carboxymethylation procedure introduced 1 carboxymethyl group onto 1 out of about 30 glucose residues in the cellulose chain. This treatment involved exposure to what were essentially mercerizing conditions before the carboxymethyl groups were added. The partial-aminoethylation procedure introduced one $—CH_2CH_2NH_2$ group onto 1 out of about 25 to 30 glucose residues. The partial-acetylation treatment introduced acetyl groups onto about one-third of the hydroxyls—*i.e.*, an average of 1 acetyl group per glucose residue. The qualitative results obtained when the chemically altered cotton pieces were soiled and washed by the usual procedures are shown in Table XII.

The washing results in Table XII represent the averaged performance of from two to five types of detergents; these did not necessarily produce a uniform effect, and in the case of the partially carboxymethylated cloth soiled in either aqueous or carbon tetrachloride dispersions and washed with an alkylarylsulfonate detergent, the effect was the opposite to that produced by four other detergents. Time did not permit a further study of the unexpectedly ineffective soil removal in this particular system.

None of these treatments produced a striking improvement in resistance to soiling, although mercerization and partial carboxymethylation definitely increased resistance to soiling from the aqueous dispersion. A more noticeable desirable effect was noted in the ease of soil removal; the partial-carboxymethylation treatment produced the most improvement in this respect (except for the alkylarylsulfonate detergent). This is of significance when considered with the favorable effects produced

by the treatment with the polyacrylate-type resin containing similar carboxylate groups. Partial carboxymethylation and partial aminoethylation are thought to produce opposite electrical charges on treated cloths, and thus it is reasonable that they would display opposite effects toward soil dispersions (especially dispersions in an ionizing liquid), as was found to be the case in these experiments. The favorable effect upon soil removal of the treatments with carboxylate materials is of further interest in connection with the enhanced detergency produced when sodium carboxymethyl cellulose is included in formulations of commercial built detergents for clothes washing.

Summary.—While some resistance to soiling from CCl_4 or aqueous dispersions was produced by a number of the treatments tried, some of these (neutral vinyl resins, hydrophobic finishes) had the effect of making the soil particles definitely more difficult to remove by washing, and therefore appeared to be unsuitable. Some others which enhanced the ease of soil removal also increased the ease with which soil was acquired (starch, cationic softeners, partial acetylation with aqueous soil, some vinyl resins), and thus were also thought unsatisfactory. The most promising treatments for cloth exposed to these liquid-dispersed soils appeared to be partial carboxymethylation, treatment with a resin bearing carboxy groups, and application of certain softeners (in addition to the effective but impractical method of having the cloth damp). It is considered significant that these most promising treatments all could confer an electrical charge and cation-exchange properties upon the cotton cloth.

Dry Soils

After most of the work with liquid-dispersed soils had been done, the relative value of studies with dry soils became increasingly apparent. This type of soil is extremely important in end-use, but has been little used in prior laboratory work because of various experimental difficulties and because most of the earlier work has been on evaluation of detergents, for which purpose soils dispersed in liquids have been considered adequate. Because of the importance in this problem of resistance of cotton cloth to dry soil, it was considered necessary to do some exploratory work on dry soiling.

Experimental Procedure.—Treated and untreated swatches of cotton cloth, in equilibrium with laboratory air at normal temperatures, were tumbled with rubber stoppers and a portion of "dry" soil (also in equilibrium with laboratory air) in a tumbling jar of the type employed for dynamic water-absorption tests on fabrics. Twenty to thirty 2-in. square swatches and twelve to fifteen No. 2 rubber stoppers made a normal load in the tumbling jar. The jar was rotated for about 15 min. in each test. Blanks of untreated cloth were included as controls in each run. In the first experiments, the tumbling treatment produced excessively heavy soiling, even when only a relatively small amount of soiling material was used. However, by reducing the quantities of soil, by shaking the soiled swatches in a sieve, and by brushing the shaken soiled pieces lightly, it was possible to minimize the excess soil and to obtain estimates of the relative extent of soiling of the test pieces. The same lampblack as employed for the liquid-dispersed soiling mixtures previously described was used as an artificial soil, and sifted, screened vacuum-sweeper dirt from a local theater was used

TABLE XIII. REFLECTANCE VALUES OF SWATCHES OF CLOTH TREATED WITH VARIOUS FINISHES, AND EXPOSED TO DRY LAMPBLACK IN A TUMBLING JAR

Treatment*	Reflectance (%)
Untreated	4
Atco Dri	0
Drax	1
Dow-Corning 1107	0
Softener #1	4
Softener #2	5
Softener #3	6
Water-soluble acrylate resin	6
Softener #4	7
Softener #5	10

* Softeners #1-5 are those of Table I.

TABLE XIV. REFLECTANCE VALUES OF SWATCHES OF CLOTH TREATED WITH VARIOUS FINISHES, AND EXPOSED TO DRY VACUUM-SWEEPER DIRT IN A TUMBLING JAR

Treatment	Reflectance (%)
Untreated	21
Atco Dri	16
Drax	19
Softener #2	20
Softener #5	22
Atco D-88	22
Softener #1	25

TABLE XV. REFLECTANCE VALUES OF SWATCHES OF PARTIALLY ACETYLATED CLOTH EXPOSED TO DRY PIGMENTS IN A TUMBLING JAR

Pigment	Treatment	Reflectance (%) after Shaking in sieve	Reflectance (%) after Shaking in sieve and brushing
Lampblack	Untreated	9	12
	Partially acetylated	18	25
Vacuum-sweeper dirt	Untreated	25	34
	Partially acetylated	35	44

TABLE XVI. QUALITATIVE EFFECT OF VARIOUS TREATMENTS ON THE EASE OF SOILING OF COTTON CLOTH BY DRY LAMPBLACK OR VACUUM-SWEEPER DIRT

Treatments which made cloth *more* resistant to soiling than the untreated cloth	Majority of softeners Water-soluble acrylate resin Mercerization Partial carboxymethylation Partial acetylation
Treatments producing no definite effect	Starch (5%) Some softeners Some resins (condensation type)
Treatments which made cloth *less* resistant to soiling than the untreated cloth	Nondurable and durable hydrophobic finishes Most resins (vinyl type)

as a representative natural soil. Although swatches soiled by the vacuum-sweeper dirt were brown in hue, rather than the usual grey to black, the relative extent of soiling of swatches exposed to this type of soil was measured on the same reflection meter with the same green (tristimulus) filter as was used in all the reflectance measurements on swatches soiled with black pigments. For test pieces, swatches treated as described previously were used.

This test method gave quite a noticeable difference in the extent of visual soiling for both of the above types of dry soil. The actual reflectance values for two typical comparative tests are given in Tables XIII and XIV.

The distinction in the extent of soiling among the various swatches tested was greater to the eye than would be indicated by the photometer readings, due to the general low level of reflectance. The eye-visible difference in extent of soiling between the untreated pieces and the pieces treated with water-repellent finishes in Table XIII, for example, was much larger than might be expected from the reflectance difference of only 3 or 4 percentage units.

From a series of comparative soiling runs like those shown in Tables XIII and XIV, it was found that the soiling behavior of treated swatches toward lampblack and toward vacuum-sweeper dirt was quite similar. The greatest resistance to soiling, for both types of dry soil, was produced by partial acetylation. Some typical values illustrating the value of this treatment are given in Table XV. The greatest susceptibility to soiling was produced by applications of neutral vinyl resins or hydrophobic finishes. The qualitative rankings of the various treatments are summarized in Table XVI.

It will be observed that among the treatments which most improved the resistance to these dry soils are several which had a favorable effect in producing resistance to the liquid-dispersed soils. As was noted before, treatments which conferred cation-exchange properties upon the cotton cellulose appear to be of especial interest. It is also worthy of note that swatches treated with neutral vinyl resins or with durable hydrophobic finishes had two soiling properties in common: (1) all were more susceptible to dry soiling than was untreated cloth; (2) after soiling from carbon tetrachloride dispersions of lampblack, all held the pigment more tenaciously upon washing. These two properties may be related to some type of preferential "wetting" or other surface-attachment phenomenon.

No washing tests have been run yet on dry-soiled swatches. More work is necessary before a conclusive answer can be given as to the correlation between resistance to liquid-dispersed soils and resistance to dry soils. Work on this project is being continued at the Institute of Textile Technology.

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Application of the Specific Gravity Gradient Column to the Quantitative Determination of Additives in a Base Material*

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Abstract

The requirements for, and limitations of, a method of quantitative estimation of additives in a base material, measured by differences in density, are set forth. The specific gravity gradient column of Linderstrom-Lang is described and discussed in terms of its range, sensitivity, stability, and calibration. The bearing which these factors have on the method is illustrated by an example in which the concentration of a melamine resin, applied to a wool flannel for control of shrinkage, is determined.

Introduction

Interest in reliable methods of determining the amount and distribution of additives in base materials has prompted the use of analytical chemical and spectroscopic, microscopic, x-ray diffraction, and radioactive-tracer procedures in the past. The problem of measuring low concentrations of resins, sizes, fillers, plasticizers, and other chemicals in textiles, rubber, plastics, and the like may not always be satisfactorily resolved by these methods, however. In some instances, for example, chemical similarity of the additive to the base material, or poor sensitivity or precision of known procedures, is encountered. Especially difficult are the determinations of uniformity of distribution, resulting when addition is made by mixing, dipping, padding, etc., and of the rate of loss of the additive by evaporation, dusting-off, leaching, or solvation. An additional means for attacking these problems, supplementing those mentioned above, would be valuable.

When chemical identification is not required, it is frequently possible to take advantage of a differ-

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ence in specific gravity between the additive and the base substance of a binary* mixture. As in all experimental procedures, there are several limitations to the applicability of the test. In this instance the main factors are: (1) that the difference in specific gravity between the base and the additive, the volume ratio of the latter to the former, and the sensitivity of the detecting means be adequate to provide the required precision; (2) that the additive and base be unaffected in composition and volume ratio by the method of measurement. (This applies also to the loss or gain of fortuitous "additives" such as water or air.) The relationships pointed out in (1) can be calculated readily from density considerations.

If W_a, V_a, and ρ_a are the weight, volume, and density, respectively, of the additive material, and if, using subscript b, the same significance holds for the base material, the three quantities will be related by the definitive equation for density:

$$W_a = \rho_a V_a, \quad \text{and} \quad W_b = \rho_b V_b. \tag{1}$$

A mixture of additive and base can be taken as an entity and can be similarly expressed, *viz.*,

$$W_a + W_b = \rho_m(V_a + V_b), \tag{2}$$

where ρ_m is the density of the combined substances. If we now substitute from equation (1) to eliminate V_a and V_b from equation (2), and also eliminate W_a and W_b by substituting the concentration, c, from

$$W_a = cW_b, \tag{3}$$

an equation will result which can be rearranged to relate the concentration to ρ_a, ρ_b, and ρ_m only, thus:

$$c = -\rho_a(\rho_b - \rho_m)/\rho_b(\rho_a - \rho_m). \tag{4}$$

The sensitivity, s, of this method of detection can be found by examining the rate at which ρ_m will change when the concentration of the additive is changed. This can be done by rearranging equation (4) to make it explicit in ρ_m, and then differentiating both sides with respect to c:

$$s = d\rho_m/dc = (\rho_a^2\rho_b - \rho_a\rho_b^2)(c\rho_b + \rho_a)^{-2}. \tag{5}$$

The quantity in the first parentheses is the most important factor in determining the sensitivity of the method. The sensitivity obviously goes to zero when $\rho_a = \rho_b$; the effect of changes in concentration, however, is generally small.

* For some purposes, several components can be considered as one if their proportions remain unchanged.

Definition

A specific gravity* gradient column is a vertical column of miscible liquids of different specific gravities which have been so mixed that the specific gravity of the mixture changes in a continuous fashion from top to bottom. It was first described by Linderstrom-Lang [3] as a convenient means for measuring the density of substances where small differentials in density required a discriminating means capable of high sensitivity.

Plotting gravity *vs.* height in the column results in a sigmoid curve wherein the center third is substantially linear. Objects dropped into the column therefore sink in the liquid until a level of the same density is reached, as shown in the photograph of a typical column (Figure 1).

Columns have been prepared in two ways. One method is to pour a series of mixtures of two liquids carefully, one above the other, into a glass tube or graduate. The mixtures are made up in proportions such that each differs from the one above and below it in the column by a desired differential in specific gravity. An easier procedure, the one used in the present discussion, is to pour equal amounts of two pure liquids, or two known mixtures thereof, one above the other in the column. In either case, the gradient smooths out by diffusion in a few hours, and is substantially stable after 24 hrs. Moderate stirring at the interface accelerates this process in the latter column.

Once prepared, a column is surprisingly durable. Changes in the gradient occur extremely slowly, making it possible to use the same column, inserting and removing specimens, for a month or more.

Many liquids can be found that will make a satisfactory column. For practical use, however, the field will be narrowed by the need for using liquids which do not interact chemically, possess fairly low viscosity and volatility, are additive by volume, and are inert to the materials to be immersed in them. Despite these restrictions, it is usually possible to find pure or mixed liquids covering a

* The terms "density" and "specific gravity" are practically equivalent when, as in this work, the specific gravities of the liquids are found in terms of water at 4°C, and when these determinations, as well as calibration and use of the columns, are conducted at a single temperature, 25°C in this instance.

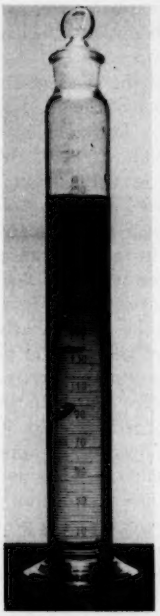

FIG. 1. *Specific gravity gradient column separating vulcanized linseed oil (ρ = 1.07 g./cc.) from tire tread stock (ρ = 1.14 g./cc.). (Half saturated NaCl and half water.)*

wide range of specific gravities as well as permitting a flexible choice of sensitivity.

Dry organic liquids can be used where moisture is to be avoided; aqueous solutions of sugar or salts may be employed where advantageous. Among the common solvents that have been used successfully are kerosene (ρ = 0.79 g./cc.), xylene (ρ = 0.855 g./cc.), bromobenzene (ρ = 1.48 g./cc.), and carbon tetrachloride (ρ = 1.58 g./cc.). Methylene iodide (ρ = 3.325 g./cc.) has been used as the heavier liquid in a column requiring high density.

Columns have been used by Boyer, Spencer, and Wiley [1] to follow polymerization and crystallization in synthetic polymers, and by Tessler, Woodberry, and Mark [6] to examine influences of spinning variables on synthetic fibers and to follow differential digestion of cellulose. Preston and Nimkar [5], who have shown the value of the method in identifying natural and synthetic fibers in mixtures, have also extended the inherent ability of the columns to provide precise data even for small particles by viewing short lengths of individual fibers through polarizing screens.

Calibration

Columns have been calibrated in three ways: by floating droplets of salt solutions of known specific gravity; by a colorimetric method, where a dye is added to one of the components; or by preparing stable solid materials of known specific gravity to rest at various levels as reference points. Preston and Nimkar [5] have suggested the use of hollow glass floats for this purpose. In special instances, refractive index determinations can also be used. The specific gravity of a sample can be found either from a curve or by interpolation, by finding its height in the column.

Floats offer several advantages which influenced their use here. For example, variation in specific gravity of a column due to small slow changes in temperature can be tolerated to a greater extent if permanent reference points are always visible in the column. This makes temperature control less of a problem.

For the illustrative textile problem to follow, floats were formed by casting selected mixtures of two polyester resins inside glass capillaries, removing them, and breaking them into convenient lengths. They were calibrated by a sink-float procedure, using precisely measured mixtures of carbon tetrachloride and xylene, carefully thermostatted. Once a satisfactory set of floats was prepared, differing in specific gravity by small amounts over the useful range, they were examined for permanence of calibration by immersing for several weeks in the solvent mixture and then recalibrating. No changes larger than experimental error were found then nor at the end of the investigation.

Stability

Coarse columns—*i.e.*, those which cover a wide range of specific gravity—are relatively less sensitive to fluctuations in temperature than are those of narrower range. Variation in temperature changes the density of each component—liquids, floats, and specimens—according to β, their cubical coefficients of thermal expansion. On the other hand, a larger difference in specific gravity from top to bottom increases the tendency for mixing; hence, the coarser columns are less stable and less durable than the

finer. Changes in temperature probably promote convective mixing.

Study of Melamine Resin on Wool

The utility of these columns for determining quantitatively the concentration of an additive on a base material was explored by attempting to measure the concentration of a melamine resin applied to a woolen cloth for control of shrinkage. Other means for attacking this problem have provided evidence that resin solids are not applied to the wool in the concentration that would be calculated from the concentration of the treating bath and the wet pickup on the cloth. However, these methods had recognized defects which weakened the conclusions.

The material for the tests was prepared by immersing swatches of unfinished 8-oz. women's-wear wool flannel in melamine resin solutions containing 0%, 2.5%, 5.0%, 7.5%, and 10.0% resin solids, causing them to pick up 100%, 108%, 96%, and 109% of the solutions, respectively, based on the dry weight of the swatch. ("Nominal" concentrations can be calculated as the products of these two figures.) All were then cured in a circulating-air oven for 9 min. at 290°F. The resin solution was also coated on a microscope slide, carefully cured to minimize the formation of bubbles, and finally scraped off and pulverized.

The limiting factors discussed earlier were instrumental in the choice of a pure, commercial mixture of xylene isomers $\left(\rho\ \frac{25°C}{4°C} = 0.85514\ \text{g./cc.}\right)$ as the less dense, and carbon tetrachloride $\left(\rho\ \frac{25°C}{4°C} = 1.58517\ \text{g./cc.}\right)$ as the more dense liquid. These encompass the density range within which are found both wool and the resin—namely, 1.3 to 1.5 g./cc.

Columns were prepared as described earlier, using stoppered 250-ml. graduates wherein the 2-ml. graduations, used in this case as a scale of height, were about 2 mm. apart. Readings could be made to a half-division.

By using exploratory columns, the density of the cured resin powder was found to be 1.4290 g./cc., and the density of the wool, 1.3169 g./cc. By means of equation (5), it could then be found that a change in resin concentration of 1% near zero would change ρ_m by 0.00100 g./cc.; near 10% concentration this rate of change would be about 0.0009 g./cc. Inasmuch as it was desired to detect a change in concentration of ½%, a column with a gradient of 0.0009 g./cc., or less, per 2-mm. division would be required.

Examination of the effect of change in temperature on the position of the floats and specimens was also carried out. For xylene and carbon tetrachloride, β is about 0.001/°C, while that for the polyester resins is only about 0.0003/°C. The coefficient for wool could not be found, but is probably not much different from those for the resins. Change in temperature of the liquids will therefore cause the system of floats and specimens to rise and fall in the column in a body, with some displacement of the wool relative to the floats. The magnitude of the error in precision resulting from a fluctuation in temperature will depend only on the latter displacement. In this instance, calculation of the error is hampered because β for wool is not known. However, it appears that a total change of 2°C would cause less than 0.05% error, or no greater than the experimental precision.

It is useful to recognize in a problem of this kind that the determination of the specific gravity figures need not be carried out to a high degree of *accuracy*, but that adequate *precision* must be maintained. This is because relative values and differentials are important to calculations in this problem, rather than determination of "absolute" densities. In this instance, the relative precision was maintained in part by calibrating the floats in the same liquids used for the columns, and at the same temperature as for the pycnometric measurement of the liquids.

Columns were prepared wherein the specific gravity gradient was 0.00030 to 0.00040 per division near the center. Because of the nonlinearity, the gradient decreases—*i.e.*, sensitivity increases—as the top or bottom is approached. These columns were made up of equal parts of a heavier mixture, consisting of 64.98% carbon tetrachloride and the remainder xylene, and a lighter mixture, containing 63.90% carbon tetrachloride. To reduce temperature effects they were kept in a conditioned room at 25° ± 1°C and were jacketed in a 5-gal. water bath to eliminate short-term fluctuations.

The total range of the columns for floating the treated wool specimens covered from about 1.312 to 1.331 g./cc., or about 0.02 unit. Figure 2 shows a calibration curve for one of these columns, illustrating also the positions of the floats, the average positions of yarn specimens (A to E) and their standard deviation in specific gravity, as well as the

TABLE I. AVERAGE SPECIFIC GRAVITY AND STANDARD DEVIATION OF YARNS FROM RESIN-TREATED WOOL FLANNEL

	Specimen designation				
	A	B	C	D	E
Nominal concentration (%)	No resin	2.5	5.4	7.2	10.9
Specific gravity (g./cc.)	1.3169	1.3192	1.3208	1.3231	1.3265
Standard deviation (g./cc.)	0.0012	0.0009	0.0012	0.0010	0.0014

TABLE II. CONCENTRATION OF RESIN ON YARN (COMPARISON OF TWO METHODS OF CALCULATION)

	B	C	D	E
1. Calculated from treatment (%)	2.5	5.4	7.2	10.9
2. Calculated from specific gravity (%)	2.3	3.9	6.4	10.2
3. Line 2/Line 1 × 100	92*	72	89	94

* Not significantly different from 100.

composition of the liquid mixtures. The cured pulverized resin required a column of higher density to include its specific gravity. This column covered the range from 1.370 to 1.430 g./cc.

The procedure followed in examining all of the wool samples was as follows: Ten short lengths of yarn were cut from random locations in each swatch, different lengths—*e.g.*, $\frac{1}{4}$ or $\frac{1}{2}$ in.—being employed in alternate swatches to identify in the columns treatment with successively increasing concentrations of resin bath. The yarns were dropped briefly in boiling xylene, to dry and to displace air, and were then immediately dropped in the lighter of the two mixtures used to make the columns. The densest of the groups of specimens was introduced into a column first, followed in sequence by the less dense. Because of fairly wide variation in density within each group, it was found advantageous in this instance to use two columns, placing alternate groups in each. This eliminated the complication of intermingling groups. Hence, one column contained yarns with nominal solids concentrations of 0%, 5.4%, and 10.9%, while the second column contained those of 2.5% and 7.2%. The resin powder was also dried and soaked in the mixture before being placed in its column.

As a result of from three to seven repetitions of these tests in different columns, and with fresh specimens in each case, the data presented in Table I were obtained for the five swatches.

Equation (4) was then used to calculate the concentrations of resin solids; these are listed on line 2 of Table II. The concentrations of resin calculated from the product of wet pickup and concentration

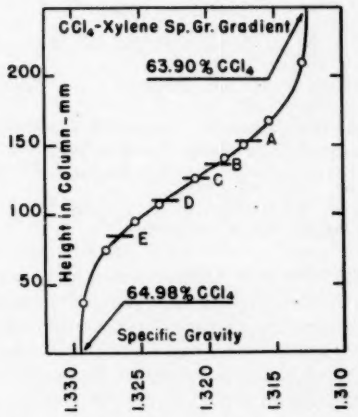

FIG. 2. *Curve for a representative column, showing positions of calibrating floats (circles) and treated wool specimens, with standard deviation (lines).*

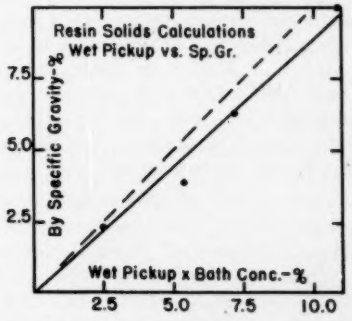

FIG. 3. *Calculated relationship between two methods of estimating concentration of melamine resin additive on wool: by wet pickup, and by specific gravity.*

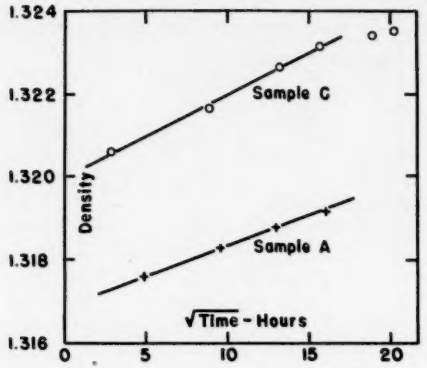

FIG. 4. *Change in density with time of two wool specimens. A—Untreated. C—3.9% resin added.*

of the bath are given on line 1. The relationship between the two sets of data are given on line 3. Hence, it is found that the resin solids retained in the flannel were not equal to those calculated from the concentration of the resin bath and the wet pickup. They appear to be proportional, however, examination of Figure 3 showing that the retention is about 87% of the assumed concentration.

Changes in Specific Gravity with Length of Immersion

An interesting side light should be pointed out which was noted during the use of this method on woolen yarns. Although it did not prove too troublesome a complication, the yarns were found to continue to change slightly in specific gravity over long periods of time in a column. It was noted that the density of wool lacking resin increased uniformly up to 200 hrs., going from 1.3169 g./cc. after 24 hrs. to a final figure of 1.3192 g./cc. Wool containing 3.9% resin solids, on the other hand, rose from 1.3208 g./cc. and was still rising 400 hrs. later, when its density was 1.3235 g./cc.

A plot of density *vs.* square root of time is shown in Figure 4. It can be seen here that at least the earlier stages are linear in these two functions, suggesting that the phenomenon may be one of diffusion. Hermans and Vermaas [2] and Preston [4] have pointed out the possibility of changes in density depending, in the first place, on the nature of surrounding medium, and, in the second place, on the existence of voids of molecular dimensions in wool and cotton, representing regions of chain termination and similar discontinuities in structure. Without more extensive inquiry than that described here, it is not possible to state with certainty which of several mobile components of the system might be diffusing alone or in combination. Increase in density with time could arise from loss of air or water from the fiber, with replacement by solvent, or by disproportionate absorption of the liquids without displacement of another substance. The molecular sizes of carbon tetrachloride and xylene (2.55 and 4.30 Å., respectively) make the latter plausible, though not exclusively so.

Acknowledgment

The authors express their thanks for the interest and assistance rendered by Dr. N. T. Woodberry and Mr. F. L. Graves, whose discussions and suggestions were instrumental in forwarding this work. Acknowledged with thanks is the support afforded by Dr. R. P. Chapman, Director of the Analytical and Testing Division, without whose permission this work could not have been carried out.

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Book Reviews

Elastomers and Plastomers—Their Chemistry, Physics and Technology: Vol. I: General Theory; Vol. II: Manufacture, Properties and Applications; Vol. III: Testing and Analysis; Tabulation of Properties. Edited by R. Houwink. Amsterdam and New York, Elsevier Publishing Co., Inc. Vol. I: 1950; 509 pages; price, $7.00. Vol. II: 1949; 531 pages; price, $7.00. Vol. III: 1948; 182 pages; price, $3.50.

(Reviewed by S. G. Weissberg, National Bureau of Standards, Washington, D. C.)

This treatise in three volumes is the collaborative product of active, internationally known specialists.

Comprising nearly half of Volume I are two well-written, extensive chapters on the organic chemistry of macromolecules, by C. Koningsberger, and the kinetics of polyreactions, by H. Wechsler, W. P. Hohenstein, and H. Mark. Although the topics overlap, the emphasis in the two chapters is different. Four chapters by G. J. von Amerongen on molecular constitution, mechanical properties, physics and structure, and polymer-liquid interaction are excellently presented from a modern, fundamental point of view. L. Hartshorn's chapter on electrophysics is a model of clear physical exposition. A chapter on plasticizers by R. S. Colborne approaches the subject from a technologic as well as thermodynamic point of view. Some of this chapter unnecessarily overlaps part of Chapter 9. The two could well have been integrated. In a chapter on mechanical operations, H. Gibello presents aspects of mechanical engineering and processing techniques common to a number of different materials. The chapter by H. A. Frank on economic aspects, which introduces the volume, is by now only of historical interest.

There is much more content in Volume II than the title suggests. Treated in detail is the chemistry as well as the manufacture, properties, and applications of phenolics, ureas and melamines, ethylene derivatives, cellulose and protein plastics, synthetic polyamides, silicones, alkyds, natural resins, asphalts, and natural and synthetic rubbers.

Volume III brings together in a convenient form methods of testing physical and chemical properties of polymers. In particular, the section on identification of polymers is extremely valuable. The last two chapters are devoted to easily used but incomplete tables of properties of polymers. A large amount of useful information scattered throughout Volume II could be incorporated into Volume III; or the latter added to Volume II as an appendix.

This set of books, with more than 2,700 literature and patent references, is a worth-while addition to the literature.

Monomers. Section II. Edited by E. R. Blout and H. Mark. London and New York, Interscience Publishers, Inc., 1951. 276 pages. Price, $5.00.

(Reviewed by S. D. Douglas, Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corp., South Charleston, W. Va.)

The remarkable increase in the commercial utilization of synthetic polymeric materials in the last few years has prompted the preparation of a large number of simple organic compounds from which macromolecules of actual or potential importance are produced by condensation or addition polymerization. The properties, reactions, and applications of these monomers have, for the most part, been well recorded in the literature, but, with the exception of those that are long established and widely used, this information is too widely scattered to be available in readily accessible form. The present compilation is therefore a successful effort to bring together pertinent data about the newer materials, including many of growing industrial importance.

Monomers is published in the form of individual pamphlets, in each of which only compounds falling into one category are considered. In this way, additions to the collection can be made as frequently as desired. An attractive feature is the uniformity with which the subject matter is presented. Each article describes, in sequence, methods of preparation, purification, and analysis, physical and chemical properties, polymerization, and copolymerization with suitable monomers, and is concluded by a bibliography. Section II covers acrylic derivatives (three articles),

vinyl ethers, vinyl pyridine, and *N*-vinyl carbazole. The editors point out that additional subjects are in preparation and that others will be considered as they become commercially important.

It is evident that to the resin chemist this series will be an extremely useful source of detailed information about many of the industry's raw materials.

Artificial Fibres. R. W. Moncrieff. New York, John Wiley & Sons, Inc., 1951. 313 + x pages. Price, $4.50.

(Reviewed by C. W. Bendigo, American Cyanamid Company, New York, N. Y.)

Confusion surrounding the many new synthetic fibers can be largely cleared up by reference to this book.

The viewpoint is admittedly British, and some fibers which we in the United States are little interested in (*viz.*, alginates) are given what appears to be a disproportionate amount of space. The book is not balanced from an American point of view but does present a good compilation of most of the fibers which one hears about today.

On each fiber a generous amount of general information is given, as well as some highly technical chemical-reaction formulas which most readers can easily skip without impairing the value of the book. The chemical equations, on the other hand, will be of interest to those who are directly interested in the chemical structure of the new synthetics.

The author, on occasion, gives his opinions regarding aspects of some of the fibers he describes. These opinions are not necessarily those shared in the United States, but they should not confuse most readers.

The organization is good. It proceeds from description of fundamental concepts of fibers through description of regenerated fibers (cellulosic, alginic, and protein) to discussion of the chemical fibers which the author terms "synthetic." The last part of the book on processing of the various fibers is sketchy, especially the section on dyeing and finishing. The very last section, on identification and estimation of synthetic fibers, should be of value to many textile technicians.

A listing of the fibers described shows the scope covered: the various rayons, alginate fibers, Azlon, nylon, Perlon, Terylene, Vinyon, Saran, Pe Ce, acrylic fiber, polythene, glass, and coated fibers.

Handbook of Weaves. G. H. Oelsner. Translated and revised by Samuel S. Dale. New York, Dover Publications, Inc., 1951. 402 + vii pages; 1875 illustrations. Price, $7.50.

(Reviewed by Prof. Edward L. Golec, Lowell Textile Institute, Lowell, Mass.)

For the experienced stylist, designer, hand-loom weaver, power-loom weaver, teacher, and advanced student this book is a most valuable source for developing new weaves, cloth structures, and textures.

Although this translation covers practically all weaves, the sections on crepe weaves, explaining 12 different methods of construction (with 342 illustrations), and on color effects (with 187 illustrations) are outstanding.

Other topics rarely found in textile-design books which are worthy of note include: breaks or recesses in the cloth, weaves that deflect certain threads, reform weaves, broché fabrics, and double transposed textures.

The chapter on analysis, although good, is too brief, especially since textile literature is sadly lacking in texts on fabric analysis.

The chapters dealing with simple drafts and the 3 basic weaves are not sufficiently complete to give the beginner a proper foundation in fabric design; therefore, this work is definitely more valuable to the experienced designer.

American Chemical Society

75th Anniversary Meeting

The American Chemical Society will hold its 120th National Meeting in New York, September 3 to 7, 1951. This meeting will recognize the 75th anniversary of the founding of the Society. Headquarters will be at the Hotel Statler. The programs scheduled for the symposia on cellulose, wood chemistry, and textiles will be held at the Waldorf-Astoria as follows:

Symposium on Fundamentals of Cellulose Chemistry

K. H. Meyer, *Honorary Chairman* H. Mark, *Chairman*

September 4, Morning Session

"Introductory Remarks," by K. H. Meyer, University of Geneva

"Early Organic Chemical Work on the Structure of Cellulose," by K. Freudenberg, University of Heidelberg

"Relative Reactivities of the Three Hydroxyl Groups in Cellulose," by C. B. Purves, McGill University

"Preparation and Structure of Polyglucose," by E. Pacsu, Princeton University

"Carboxyl Groups in Cellulose Materials," by G. F. Davidson, Shirley Institute

"Principles of the Formation of Cellulose Derivatives," by G. Champetier, École Supérieure de Physique et de Chimie, Paris

September 4, Afternoon Session

"Intrinsic Viscosity and Molecular Weight of Cellulose in Solution," by C. M. Conrad and Kyle Ward, Southern Regional Research Laboratory, U.S.D.A.

"Polymolecularity of Cellulose in Solution," by S. Claesson, University of Uppsala

"Mechanism of Swelling and Solution of Cellulose and Its Derivatives," by H. M. Spurlin, Hercules Powder Company

"General Relation of Different Types of Cellulose Degradation," by Milton Harris, Harris Research Laboratories

"Mechanism of Deformation of Cellulose and Its Derivatives," by O. Kratky, University of Graz, Austria

September 5, Morning Session

"Submicroscopic Structure of Native Cellulose Compared with That of Starch," by K. H. Meyer, University of Geneva

"Study of the Crystalline-Amorphous System with X-Rays," by P. H. Hermans, Cellulose Research Institute, Utrecht, Holland

"Evaluation of Experimental Data Concerning the Super-Molecular Structure of Cellulose," by J. A. Howsmon, American Viscose Company

"Effect of the Crystalline-Amorphous System on the Mechanism of Degradation," by W. E. Roseveare, Du Pont

"Interaction of Water with Cellulose in Wood and in the Pure State," by A. J. Stamm, Forest Products Laboratory, U.S.D.A.

"Remarks on Vitreous Cellulose," by O. Bryde, The Norwegian Pulp and Paper Research Institute, Oslo

"Concluding Remarks," by H. Mark, Polytechnic Institute of Brooklyn

Symposium on Wood Chemistry

E. Hägglund, *Honorary Chairman* Harry F. Lewis, *Chairman*

September 6, Morning Session

"Introductory Remarks," by E. Hägglund, Swedish Forest Products Research Laboratory

"Biological Processes in the Formation of Wood," by I. W. Bailey, Harvard University

"The Structure of Wood and Bast Fibers," by K. Mühlethaler, Tech. Hochschule, Zurich

"The Nature and Distribution of Wood Extractives and Their Relation to Wood Species," by Holger Erdtman, Royal Institute of Technology, Stockholm

"The Present Status of the Chemistry of Cellulose," by E. Heuser, Research Associate Emeritus of The Institute of Paper Chemistry

September 6, Afternoon Session

"The Hemicelluloses and Their Significance in Wood Fibers," by J. K. N. Jones, University of Bristol

"The Nature of Lignin," by K. Freudenberg, Heidelberg University

"The Chemistry of the Pulping Process," by Rodger Dorland, Abitibi Power and Paper Co., Ltd., Canada

"The Fine Structure of Fibers and Their Papermaking Properties," by Börje Steenberg, Swedish Forest Products Research Laboratory

Symposium on Textiles

Milton Harris, *Chairman*

September 7, Morning Session

"Introductory Remarks," by Milton Harris, Harris Research Laboratories

"Liveliness of Fabrics as Related to Fiber Properties," by J. W. Ballou, Du Pont

"Luster as Related to Molecular Structure of Fibers," by Lyman Fourt and Arnold M. Sookne, Harris Research Laboratories

"Fundamentals of Flame Retardancy," by Robert W. Little, Hercules Powder Co.

"Infrared Barriers (metallic finishes) in Clothing from Physiological and Practical Points of View," by L. P. Herrington, John B. Pierce Foundation, New Haven, Conn.

September 7, Afternoon Session

"The Macromolecular Structure of Wool," by Peter Alexander, Chester Beatty Research Institute, The Royal Cancer Hospital, London

"Fundamentals of Dyeing Cellulosic Fibers," by Harold R. McCleary, American Cyanamid Co.

"Stabilization of Cotton Fabrics Against Shrinkage in Laundering," by Edward C. Pfeffer, Jr., Cluett, Peabody & Co., Inc.

"Modification of Viscose Fiber Properties to Achieve Dimensional Stability," by Jack Epelberg, Cluett, Peabody & Co., Inc.

"Influence of Fiber Properties and Fabric Structure on Dimensional Stability of Wool Fabrics," by Herman Bogaty and Milton Harris, Harris Research Laboratories

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